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(54) HIGHLY MAGNETIC MATERIAL AND MANUFACTURE THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a highly magnetic material produced at low cost and having at least high magnetism and good temperature characteristics.

SOLUTION: A high magnetic material having a coercive force of not less than 1 kOe is made from an alloy comprising one or more element T selected from the group of Fe, Co, Ni, one or more rare-earth element R, and an element B, and having an amorphous phase as a main phase by a melt quenching method and then by heat-treating the alloy at a rising temperature of not less than 10 K/min.

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CLAIMS

[Claim(s)]

[Claim 1] A hard magnetic material whose coercive force it comes to heat-treat an alloy which makes an amorphous phase the main phase immediately after quenching with the above programming rate by 10K/including one or more sorts of elements T, and elements R and B which consist of one or more sorts in rare earth elements among Fe, Co, and nickel, and is 1 or more kOes.

[Claim 2] A hard magnetic material whose coercive force which it comes to heat-treat an alloy which makes an amorphous phase the main phase immediately after quenching with the above programming rate by 10K/, and comes to contain a software magnetism phase of 1 or less kOe of coercive force and a hard magnetism phase of 1 or more kOes of coercive force more than 10vol(s)(volume) %, respectively is 1 or more kOes.

[Claim 3] A hard magnetic material whose coercive force in which come to heat-treat an alloy which makes an amorphous phase the main phase immediately after quenching with the above programming rate by 10K/, and a magnetic phase and Curie temperature of 600 degrees C or more come for Curie temperature to contain a magnetic phase of 600 degrees C or less more than 10vol(s)(volume) %, respectively is 1 or more kOes.

[Claim 4] A hard magnetic material obtained after heat treatment with the above programming rate by said 10K/in a hard magnetic material according to claim 1 to 3 is a hard magnetic material characterized by including a fine crystalline phase of 100nm or less of diameters of average crystal grain as a main phase.

[Claim 5] A hard magnetic material characterized by coming to heat-treat an alloy which makes an amorphous phase the main phase immediately after quenching with the above programming rate by 100K/in a hard magnetic material according to claim 1 to 4.

[Claim 6] A hard magnetic material according to claim 1 to 5 is a hard magnetic material characterized by an absolute value of a temperature coefficient of magnetization when using it in a configuration from which a permeance coefficient becomes ten or more being as follows [0.10% / K].

[Claim 7] A hard magnetic material according to claim 1 to 6 is a hard magnetic material characterized by coercive force being the thing of 2 or more kOes.

[Claim 8] A hard magnetic material according to claim 1 to 7 is a hard magnetic material characterized by being [of residual magnetization (Ir) to saturation magnetization (Is)] 0.6 or more things comparatively (Ir/Is).

[Claim 9] A hard magnetic material according to claim 1 to 8 is a hard magnetic material which has the following empirical formula and is characterized by residual magnetization (Ir) being the thing of 100 or more emu/g.

While $T_xM_yR_zB_w$, however T express one or more sorts of elements among Fe, Co, and nickel, M expresses one or more sorts of elements among Zr, Nb, Ta, and Hf and R expresses one or more sorts of elements among rare earth elements, x which shows a presentation ratio, and y, z and w are atomic %s, and are $50 \leq x \leq 92$, $0 \leq y \leq 15$, $3 \leq z \leq 20$, and $3 \leq w \leq 20$.

[Claim 10] x which shows a presentation ratio in said empirical formula, and y, z and w are a hard magnetic material according to claim 9 characterized by being atomic % and being $86 \leq x \leq 92$, $0.5 \leq y \leq 3$, $3 \leq z \leq 7$, and $3 \leq w \leq 7$.

[Claim 11] A hard magnetic material according to claim 1 to 8 is a hard magnetic material characterized by having the following empirical formula.

TxMyRzBwEv, however T express one or more sorts of elements among Fe, Co, and nickel. M expresses one or more sorts of elements among Zr, Nb, Ta, and Hf, and R expresses one or more sorts of elements among rare earth elements. While E expresses one or more sorts of elements among Cr, aluminum, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, and germanium, x which shows a presentation ratio, and y, z, w and v are atomic %s, and are $50 \leq x \leq 10$, $0 \leq y \leq 10$, $3 \leq z \leq 15$, $3 \leq w \leq 20$, and $0 \leq v \leq 10$.

[Claim 12] x which shows a presentation ratio in said empirical formula, and y, z, w and v are a hard magnetic material according to claim 11 characterized by being atomic % and being $80 \leq x \leq 92$, $1 \leq y \leq 5$, $4 \leq z \leq 10$, $3 \leq w \leq 7$, and $0 \leq v \leq 5$.

[Claim 13] A hard magnetic material characterized by coming to carry out 0.5- pentatomic % addition of the Si in T element substitute in a hard magnetic material according to claim 1 to 12.

[Claim 14] A manufacture method of a hard magnetic material characterized by having a process which heat-treats this alloy with the above programming rate by 10K/after producing an alloy which makes an amorphous phase the main phase with a melt quenching method including one or more sorts of elements T, and elements R and B which consist of one or more sorts in rare earth elements among Fe, Co, and nickel.

[Claim 15] A manufacture method of a hard magnetic material characterized by depositing a fine crystalline phase of 100nm or less of diameters of average crystal grain as a main phase in this alloy by heat-treating an alloy which makes the main phase an amorphous phase produced with a melt quenching method in a manufacture method of a hard magnetic material according to claim 14 with the above programming rate by 10K/.

[Claim 16] A manufacture method of a hard magnetic material characterized by heat-treating an alloy which makes the main phase an amorphous phase obtained by melt quenching method in a manufacture method of a hard magnetic material according to claim 14 to 15 with the above programming rate by 100K/.

[Claim 17] A manufacture method of a hard magnetic material characterized by heat-treating an alloy which makes the main phase an amorphous phase which has the following empirical formula in a manufacture method of a hard magnetic material according to claim 14 to 16.

While TxMyRzBw, however T express one or more sorts of elements among Fe, Co, and nickel, M expresses one or more sorts of elements among Zr, Nb, Ta, and Hf and R expresses one or more sorts of elements among rare earth elements, x which shows a presentation ratio, and y, z and w are atomic %s, and are $50 \leq x \leq 15$, $3 \leq y \leq 20$, and $3 \leq z \leq 20$.

[Claim 18] x which shows a presentation ratio in said empirical formula, and y, z and w are the manufacture method of a hard magnetic material according to claim 17 characterized by being atomic % and being $86 \leq x \leq 92$, $0.5 \leq y \leq 3$, $3 \leq z \leq 7$, and $3 \leq w \leq 7$.

[Claim 19] A manufacture method of a hard magnetic material characterized by heat-treating an alloy which makes the main phase an amorphous phase which has the following empirical formula in a manufacture method of a hard magnetic material according to claim 14 to 16.

TxMyRzBwEv, however T express one or more sorts of elements among Fe, Co, and nickel. M expresses one or more sorts of elements among Zr, Nb, Ta, and Hf, and R expresses one or more sorts of elements among rare earth elements. While E expresses one or more sorts of elements among Cr, aluminum, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, and germanium, x which shows a presentation ratio, and y, z, w and v are atomic %s, and are $50 \leq x \leq 10$, $0 \leq y \leq 10$, $3 \leq z \leq 15$, $3 \leq w \leq 20$, and $0 \leq v \leq 10$.

[Claim 20] x which shows a presentation ratio in said empirical formula, and y, z, w and v are the manufacture method of a hard magnetic material according to claim 19 characterized by being atomic % and being $80 \leq x \leq 92$, $1 \leq y \leq 5$, $4 \leq z \leq 10$, $3 \leq w \leq 7$, and $0 \leq v \leq 5$.

[Claim 21] A manufacture method of a hard magnetic material characterized by heat-treating an alloy which did 0.5- pentatomic % addition of Si in T element substitute into an alloy which makes said amorphous phase the main phase in a manufacture method of a hard magnetic material according to claim 14 to 20.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the hard magnetic material excellent in the magnetic engine performance which can be used for sensors, such as a magnetic type encoder and a potentiometer, a motor, an actuator, a loudspeaker, etc., and its manufacture method.

[0002]

[Description of the Prior Art] As a magnet material which generally has the engine performance superior to a ferrite magnet or an Alnico alloy (A1-nickel-Co-Fe system), the Sm-Co system magnet, the Nd-Fe-B system magnet, etc. are known, and also many researches of an alloy magnet with a new Sm-Fe-N system magnet etc. are also made aiming at the high engine performance.

[0003]

[Problem(s) to be Solved by the Invention] However, in these magnet materials, since Nd beyond 10at% or Sm beyond 8at% was required and there was much amount of the expensive rare earth elements used, there was a defect that a manufacturing cost will become high rather than a ferrite magnet or an alnico magnet. Furthermore, since a Nd-Fe-B system magnet had a large change of the magnetic properties by temperature, it had the problem that it could not be used as a sensor. Moreover, although the Sm-Co system magnet was a magnet with the small absolute value of the temperature coefficient of magnetization, since it was a magnet more expensive than a Nd-Fe-B system magnet, the range which can be used was restricted. On the other hand, although cost was low compared with the rare earth magnet as mentioned above, since the absolute value of the temperature coefficient of magnetization was large, the ferrite magnet had the problem that it could not be used as a sensor. Moreover, although cost was low, since coercive force was small, utilization was difficult [the absolute value of the temperature coefficient of magnetization of the Alnico alloy (A1-nickel-Co-Fe system) magnet was small, and]. For this reason, it had ***** more than a ferrite magnet at least by low cost, and an appearance of the magnet material in which the temperature characteristic was further excellent was desired.

[0004] Then, invention-in-this-application persons are performing patent application in Japanese Patent Application No. No. 68822 [eight to], Japanese Patent Application No. 8-242356, etc., in order to obtain the hard magnetic material which shows high ***** by low cost. The element M which according to the technology indicated by such patent application uses Fe as a principal component and consists of one sort or two sorts or more in Zr, Nb, Ta, and Hf After producing the amorphous alloy containing the elements R and B which consist of one sort in rare earth elements, or two sorts or more using a melt quenching method, this amorphous alloy is heat-treated at 600-900 degrees C. By depositing the fine crystal phase of 100nm or less of diameters of average crystal grain which make a subject Fe of bcc, and the compound of Fe-B and/or R2Fe 14B1 The hard magnetic material 170 - 400 kA/m and the maximum magnetic energy product ((BH) max) indicate [residual magnetization (Ir) / 0.8-1.3T, and coercive force (iHc)] the comparatively high ***** of 60 - 110 kJ/m³ to be can be manufactured. By the radical of research of the above alloys, this invention persons The programming rate of the alloy which makes an amorphous phase the main phase as a result of repeating various examination and experiments by low cost paying attention to the programming rate at the time of heat-treating the alloy which makes the amorphous phase after quenching the main phase especially, in order to manufacture the hard magnetic material

excellent in *****. With the nano crystal structure (especially diameter of crystal grain of a bcc-Fe phase) of a fine crystal phase and ***** which deposit by heat treatment, it discovered that there was correlation and this invention was reached. Furthermore, in order to manufacture the hard magnetic material excellent in the temperature characteristic, as a result of repeating various examination and experiments, this invention persons discovered that a permeance coefficient (p) and the temperature coefficient of magnetization had correlation, and reached this invention.

[0005] It aims at enabling it to offer the hard magnetic material which this invention was made in view of the above-mentioned situation, was equipped with ***** excellent in low cost at least, and was equipped with the further excellent temperature characteristic.

[0006]

[Means for Solving the Problem] Among Fe, Co, and nickel, including one or more sorts of elements T, and the elements R and B which consist of one or more sorts in rare earth elements, it came to heat-treat an alloy which makes an amorphous phase the main phase immediately after quenching with the above programming rate by 10K/, and this invention made a hard magnetic material whose coercive force is 1 or more kOes a solution means of the above-mentioned technical problem. Moreover, it came to heat-treat an alloy which makes an amorphous phase the main phase immediately after quenching with the above programming rate by 10K/, and this invention made a hard magnetic material whose coercive force which comes to contain a software magnetism phase of 1 or less kOe of coercive force and a hard magnetism phase of 1 or more kOes of coercive force more than 10vol(s)(volume) %, respectively is 1 or more kOes a solution means of the above-mentioned technical problem. Moreover, a magnetic phase and Curie temperature of 600 degrees C or more made a hard magnetic material whose coercive force in which come to heat-treat an alloy with which this invention makes an amorphous phase the main phase immediately after quenching with the above programming rate by 10K/, and Curie temperature comes to contain a magnetic phase of 600 degrees C or less more than 10vol(s)(volume) %, respectively is 1 or more kOes a solution means of the above-mentioned technical problem.

[0007] As for a hard magnetic material obtained after heat-treating an alloy which makes an amorphous phase the main phase immediately after the above-mentioned quenching with the above programming rate by 10K/, it is desirable that a fine crystalline phase of 100nm or less of diameters of average crystal grain is included as a main phase. As for an alloy which makes an amorphous phase the main phase immediately after the above-mentioned quenching, it is desirable to be heat-treated with the above programming rate by 100K/. As for a hard magnetic material of the above-mentioned configuration, it is desirable that an absolute value of a temperature coefficient of magnetization when using it in a configuration from which a permeance coefficient becomes ten or more is as follows [0.10% / K]. As for a hard magnetic material of the above-mentioned configuration, it is desirable that coercive force is the thing of 2 or more kOes. As for a hard magnetic material of the above-mentioned configuration, it is desirable that they are [of residual magnetization (Ir) to saturation magnetization (Is)] 0.6 or more things comparatively (Ir/Is).

[0008] A hard magnetic material of the above-mentioned configuration has the following empirical formula, and it is desirable that residual magnetization (Ir) is the thing of 100 or more emu/g.

While $TxMyRzBw$, however T express one or more sorts of elements among Fe, Co, and nickel, M expresses one or more sorts of elements among Zr, Nb, Ta, and Hf and R expresses one or more sorts of elements among rare earth elements, x which shows a presentation ratio, and y, z and w are atomic %s, and are $50 \leq x, 0 \leq y \leq 15, 3 \leq z \leq 20$, and $3 \leq w \leq 20$. Furthermore, x which shows a presentation ratio in the above-mentioned empirical formula, and y, z and w are atomic %s, and it is desirable that it is $86 \leq x \leq 92, 0.5 \leq y \leq 3, 3 \leq z \leq 7$, and $3 \leq w \leq 7$.

[0009] Moreover, a hard magnetic material of the above-mentioned configuration may have the following empirical formula.

$TxMyRzBwEv$, however T express one or more sorts of elements among Fe, Co, and nickel. M expresses one or more sorts of elements among Zr, Nb, Ta, and Hf, and R expresses one or more sorts of elements among rare earth elements. While E expresses one or more sorts of elements among Cr, aluminum, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, and germanium, x which shows a presentation ratio, and y, z, w and v are

atomic %s, and are $50 \leq x \leq 10$, $0 \leq y \leq 10$, $3 \leq z \leq 15$, $3 \leq w \leq 20$, and $0 \leq v \leq 10$. Furthermore, x which shows a presentation ratio in the above-mentioned empirical formula, and y, z, w and v are atomic %s, and it is desirable that it is $80 \leq x \leq 92$, $1 \leq y \leq 5$, $4 \leq z \leq 10$, $3 \leq w \leq 7$, and $0 \leq v \leq 5$. Moreover, 0.5- pentatomic % addition of Si may be done in T element substitute at a hard magnetic material of this invention.

[0010] In order to solve the above-mentioned technical problem a manufacture method of a hard magnetic material of this invention The element R which consists or more of one of one or more sorts of Elements T and rare earth elements of Fe, Co, and the nickel By having a process which heat-treats this alloy with the above programming rate by 10K/, after producing an alloy which makes an amorphous phase the main phase with a melt quenching method including B A diameter of average crystal grain of a bcc-Fe phase of a fine crystalline phase which deposits in the above-mentioned alloy makes it detailed. The switched connection property of a software magnetism phase (bcc(body-centered cubic structure)-Fe) and a hard magnetism phase (R2Fe14B) improves by this. Residual magnetization (Ir), a square shape ratio.(Ir/Is), coercive force (iHc), and the maximum magnetic energy product ((BH) max) increase, and a hard magnetic material excellent in ***** is obtained.

[0011] Moreover, in a manufacture method of a hard magnetic material of the above-mentioned configuration, it is desirable to deposit a fine crystalline phase of 100nm or less of diameters of average crystal grain as a main phase in an alloy by heat-treating an alloy which makes the main phase an amorphous alloy produced with a melt quenching method with the above programming rate by 10K/. Furthermore, in a manufacture method of a hard magnetic material of the above-mentioned configuration, it is desirable to consider a programming rate at the time of heat-treating an alloy which makes the main phase an amorphous phase obtained by melt quenching method as the above by 100K/.

[0012] It is desirable to use an alloy which makes the main phase an amorphous phase which has the following empirical formula as an alloy heat-treated with the above-mentioned programming rate. While $T_xM_yR_zB_w$, however T express one or more sorts of elements among Fe, Co, and nickel, M expresses one or more sorts of elements among Zr, Nb, Ta, and Hf and R expresses one or more sorts of elements among rare earth elements, x which shows a presentation ratio, and y, z and w are atomic %s, and are $50 \leq x \leq 15$, $3 \leq z \leq 20$, and $3 \leq w \leq 20$. x which shows a presentation ratio in an empirical formula of an alloy used here, and y, z and w are atomic %s, and it is desirable that it is $86 \leq x \leq 92$, $0.5 \leq y \leq 3$, $3 \leq z \leq 7$, and $3 \leq w \leq 7$.

[0013] Moreover, an alloy which makes the main phase an amorphous phase which has the following empirical formula as an alloy heat-treated with the above-mentioned programming rate may be used. $T_xM_yR_zB_wE_v$, however T express one or more sorts of elements among Fe, Co, and nickel. M expresses one or more sorts of elements among Zr, Nb, Ta, and Hf, and R expresses one or more sorts of elements among rare earth elements. While E expresses one or more sorts of elements among Cr, aluminum, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, and germanium, x which shows a presentation ratio, and y, z, w and v are atomic %s, and are $50 \leq x \leq 10$, $0 \leq y \leq 10$, $3 \leq z \leq 15$, $3 \leq w \leq 20$, and $0 \leq v \leq 10$. x which shows a presentation ratio in an empirical formula of an alloy used here, and y, z, w and v are atomic %s, and it is desirable that it is $80 \leq x \leq 92$, $1 \leq y \leq 5$, $4 \leq z \leq 10$, $3 \leq w \leq 7$, and $0 \leq v \leq 5$. Moreover, an alloy which did 0.5- pentatomic % addition of Si in T element substitute may be used for an alloy which makes an amorphous phase of the above-mentioned presentation the main phase as an alloy heat-treated with the above-mentioned programming rate.

[0014]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained in detail. It comes to heat-treat the alloy with which the hard magnetic material concerning this invention makes an amorphous phase the main phase immediately after quenching including one or more sorts of elements T, and the elements R and B which consist of one or more sorts in rare earth elements among Fe, Co, and nickel with the above programming rate by 10K/, and coercive force is the thing of 1 or more kOes. The hard magnetic material obtained after heat treatment with the above programming rate by 10K/in the alloy which makes the above-mentioned amorphous phase the main phase contains the fine crystalline phase of 100nm or less of diameters of average crystal grain as a main phase. As for this fine crystalline phase, the

bcc-Fe phase of 100nm or less of diameters of average crystal grain and the R2Fe14 B phase of 100nm or less of diameters of average crystal grain deposit. Moreover, this hard magnetic material forms the nano diplophase organization of the fine crystalline phase which makes a subject a bcc-Fe phase, above-mentioned R2Fe14 B phase, and above-mentioned Fe3 B phase, and the amorphous phase which remained. [0015] Furthermore, as for the hard magnetic material of this invention, it is desirable to come to contain the software magnetism phase of 1 or less kOe of coercive force and the hard magnetism phase of 1 or more kOes of coercive force more than 10vol(s)(volume) %, respectively at the point which can be equipped with the middle property of a software magnetism phase and a hard magnetism phase. Although the coercive force of an alloy becomes it large that the software magnetism phase of 1 or less kOe of coercive force is under 10vol(s)(volume) %, since the concentration of rare earth elements required to constitute a hard magnetism phase becomes high, it is not desirable. Moreover, since the coercive force of an alloy becomes it small that the hard magnetism phase of 1 or more kOes of coercive force is under 10vol(s)(volume) %, it is not desirable.

[0016] moreover, the point that it can be equipped with the middle property of a software magnetism phase and a hard magnetism phase that the magnetic phase and Curie temperature of 600 degrees C or more come for Curie temperature to contain [the hard magnetic material of this invention] the magnetic phase of 600 degrees C or less more than 10vol(s)(volume) %, respectively -- ** -- it is desirable. Since the Curie temperature of a bcc-Fe phase is near 770 degree C and the Curie temperature of R2Fe14 B phase is near 315 degree C, in order for it to have two phases of the software magnetism phase and hard magnetism phase to which the hard magnetic material of this invention participates in magnetization and which are a phase, the magnetic phase and Curie temperature of 600 degrees C or more need to contain [Curie temperature] the magnetic phase of 600 degrees C or less. The temperature change of the absolute value of magnetization of each magnetic phase can have the feature that the temperature change of the magnetization by the high permeance becomes small, if the one where the Curie temperature of the phase is higher is small and contains the phase (software magnetism phase) with a high Curie temperature more than 10vol(s)(volume) % in this way. Since the temperature change of the magnetization when using that it is under 10vol(s)(volume) % by the comparatively high permeance becomes large, the magnetic phase of 600 degrees C or more does not have a desirable Curie temperature. Moreover, since a hard magnetism phase decreases that Curie temperature is [the magnetic phase of 600 degrees C or less] under 10vol(s)(volume) %, coercive force becomes low and is not desirable.

[0017] As for the alloy which makes an amorphous phase the main phase immediately after the above-mentioned quenching, in the hard magnetic material concerning this invention, it is desirable to be heat-treated with the above programming rate by 100K/at the point which makes fine the diameter of average crystal grain of bcc-Fe, and raises *****.

[0018] By the way, the property of a magnet material is expressed by the portion of the 2nd quadrant of a hysteresis curve, i.e., a demagnetization curve. Since the magnet material after magnetization is the magnetic field of the reverse sense which own residual magnetization builds, and under an anti-magnetic field, the operating point (the flux density (B) and the demagnetizing field (H) of a material) is given by one point p on a demagnetization curve. The line (OP) between a permeance coefficient (p), and p and Zero O is called a permeance line for the value (non-dimensionality) of B/mu OH here. If this permeance coefficient (p) or a permeance line will become small if magnetization lay length becomes short depending on a magnetic configuration, and it becomes long, it will become large. Between a permeance coefficient and a demagnetization factor (N), it is the following type (I).

$$p = (1-N) / N \dots (I)$$

It comes out and there is relation shown. Therefore, if the configurations of a demagnetization curve and a magnet material are given, the operating point (B, H) will be determined. The energy of a static magnetic field which the magnet material builds outside is the following type (II).

$$U = BHV/2 \dots (II)$$

(-- V is given by volume) of a magnetic material among a formula. If the configuration of a magnet material changes, since an anti-magnetic field, i.e., a permeance line, will change, the operating point p changes and

the value of Above U changes. The value of U serves as max in a certain operating point pm the middle, and the product of (BH) at that time is the maximum magnetic energy product ((BH) max).

[0019] When using the hard magnetic material concerning this invention for a sensor etc., it is desirable that the absolute value of the temperature coefficient of the magnetization when using it by ten or more permeance coefficients is as follows [0.10% / K]. It is desirable to use the thing (what has the small temperature change of magnetization), i.e., what, has the small absolute value of the temperature coefficient of magnetization and in which the temperature characteristic is excellent, when using a hard magnetic material for a sensor etc. Since the absolute value of the temperature coefficient of the magnetization when using the hard magnetic material of this invention in a configuration from which a permeance coefficient becomes ten or more becomes small below 0.10% / K It can be used suitable for a sensor etc., and if a permeance coefficient uses it in less than ten configuration, the absolute value of the temperature coefficient of magnetization will become large. Moreover, as for the hard magnetic material of this invention, it is more desirable to use it in a configuration from which a permeance coefficient becomes 20 or more at the point that the absolute value of the temperature coefficient of magnetization becomes below 0.08% / K.

[0020] The hard magnetic material of this invention excellent in such the temperature characteristic By Co being made to be contained in 0.5 – pentatomic % (at%) addition or T element in Si element T element substitute 0.5 to 20% so that it may mention later The absolute value of the temperature coefficient of the magnetization at the time or more of $p=10$ can realize a small thing below 0.10% / K to the magnet (the temperature coefficient at the time of $p=10 - 0.11 - -0.13\% / K$) of the conventional Nd-Fe-B system. Furthermore, the hard magnetic material of this invention is cheaper than the Sm-Co system magnet with which the temperature characteristic is used as a good thing from the former greatly [coercive force] from the ferrite magnet or the alnico magnet.

[0021] Furthermore, as for the hard magnetic material concerning this invention, it is desirable that coercive force is the thing of 2 or more kOes. Moreover, as for the hard magnetic material concerning this invention, it is desirable that it comes out comparatively and a certain square shape ratios (Ir/Is) are [of the residual magnetization (Ir) to saturation magnetization (Is)] 0.6 or more things. Here, the saturation magnetization (Is) in this invention is a value in case magnetization of a sample is saturated mostly, when a magnetization curve is measured under a sufficiently high external magnetic field. Control of the diameter of average crystal grain of the crystalline substance phase in the above hard magnetic materials and the concentration of each atom in each phase is realizable by controlling the heat treatment conditions at the time of heat-treating an amorphous alloy and obtaining a hard magnetic material. Heat treatment conditions are a programming rate, heat treatment temperature (annealing temperature), its holding time, etc.

[0022] The hard magnetic material concerning this invention can be expressed with the following empirical formulas.

T in the $T_xM_yR_zB_w$ above-mentioned empirical formula expresses one or more sorts of elements among Fe, Co, and nickel. These elements are the principal components of the hard magnetic material concerning this invention, and are elements which bear magnetism. If the presentation ratio x of T is made to increase, saturation magnetization (Is) will increase in connection with it. In order to realize high residual magnetization (Ir) of 100 or more emu/g, 130 emu/g at least needs saturation magnetization (Is), it is desirable to make concentration of T more than 50at%, for filling this, and in order to obtain the still higher residual magnetization (Ir) of 120 or more emu/g, as for the concentration of T, it is desirable that it is a range beyond 86at% preferably 80at(s)%. Moreover, in order to obtain outstanding ***** as for the concentration of T, considering as less than [92at%] is desirable. In the hard magnetic material of this invention, it is required to contain Fe as some elements [at least] T. In addition, if the densities of the sample in the example of this invention are about 7.6 g/cm³, for example, are 100 emu/g, they are convertible with $100(\text{emu/g}) \times 4 \times 7.6(\text{g/cm}^3) \times 0.0001 = 0.95(\text{T})$, so that it may mention later. Therefore, when it writes by emu/g, it can be regarded as magnetization of the material proper.

[0023] M in the above-mentioned empirical formula expresses one or more sorts of elements among Zr, Nb, Ta, and Hf, and these elements have high amorphous organization potency. In the hard magnetic material

concerning this invention, by adding M, also when rare earth elements (R) are low concentration, an amorphous phase can be formed. If the presentation ratio y of M is made to increase in rare-earth-elements (R) substitute, although residual magnetization (Ir) increases in connection with it, coercive force (iHc) will decline and it will change from ***** to soft magnetic characteristics. Moreover, if an amorphous formation element (M) is made to increase in the element (T) substitute which bears magnetism, reduction of saturation magnetization (Is) and residual magnetization (Ir) will arise. Therefore, in order to obtain good ***** it is desirable less than [more than 0at%15at%] and to make concentration (y) of M into the range not more than 0.5at%3at% preferably.

[0024] R in the above-mentioned empirical formula expresses one or more sorts of elements of the rare earth metals (Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). Intermetallic-compound R₂Fe 14B1 which deposits when the amorphous alloy containing R, and Fe and B is heated at a suitable temperature of the range of 873–1173K gives ***** excellent in the material of this invention. If the presentation ratio z of R is made to increase, saturation magnetization (Ir) will decrease in connection with it. In order to obtain the high residual magnetization (Ir) of 100 or more emu/g, 130 emu/g at least needs saturation magnetization (Is), and it is desirable for filling this less than [20at%] and to make concentration (z) of R into the range not more than 7at% preferably. Moreover, it is an element which is easy to form an amorphous substance, and since it cannot obtain a good amorphous phase or a fine crystalline phase if the presentation ratio of R of R is too small, it is desirable [R] to carry out to more than 3at% as concentration of R. If a part or all of R is furthermore constituted from Nd and/or Pr, still higher ***** will be obtained.

[0025] B in the above-mentioned empirical formula is an element which is easy to form an amorphous substance. Moreover, compound R₂Fe14B which deposits when the amorphous phase containing Fe and B is heat-treated at a suitable temperature of the range of 873–1173K gives ***** to the material of this invention. In order to obtain a good amorphous phase or a fine crystalline phase, it is desirable to make concentration of B into the range beyond 3at%, but since saturation magnetization (Is), residual magnetization (Ir), and coercive force (iHc) decrease with the increment in the presentation ratio (w) of B, in order to obtain good ***** it is desirable less than [20at%] and to make concentration of B into the range not more than 7at% preferably.

[0026] Moreover, one or more sorts of elements E may be added by the hard magnetic material of this invention among Cr, aluminum, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, and germanium, and the hard magnetic material in that case can be expressed with the following empirical formula to it. TxMyRzBwEv — as for the concentration x of the element T which bears the magnetism in this case, it is desirable to carry out to more than 50at% at the point to which saturation magnetization (Is) is made to increase in order to obtain the high residual magnetization of 100 or more emu/g, in order to be compatible in the still higher residual magnetization (Ir) of 120 or more emu/g, and outstanding ***** less than [more than 80at%92at%] is desirable, and it is less than [more than 86at%92at%] more preferably. In order to obtain good ***** it is less than [more than 1at%5at%] more preferably, and less than [more than 0at%10at%] and in order to realize high residual magnetization (Ir) of 120 or more emu/g, it is preferably desirable [the concentration of M in the above-mentioned empirical formula] to consider as less than [more than 0.5at%3at%].

[0027] In order to obtain an amorphous phase good in order to give ***** excellent in the material of this invention, or a fine crystalline phase, it is less than [more than 4at%10at%] more preferably, and less than [more than 3at%15at%] and in order to realize high residual magnetization (Ir) of 120 or more emu/g, it is preferably desirable [the concentration of R in the above-mentioned empirical formula] to consider as less than [more than 3at%7%]. In order to obtain a good amorphous phase or a fine crystalline phase, as for the concentration of B in the above-mentioned empirical formula, it is desirable to carry out to more than 3at%. moreover — in order to obtain good ***** — the concentration of B — desirable — less than [20at%] — it may be less than [7at%] more preferably. The corrosion resistance of a hard magnetic material improves by adding Element E. however — since ***** will deteriorate if the concentration of Element E is too high — the concentration of E — desirable — less than [10at%] — it may be less

than [5at%] more preferably. moreover -- in order to acquire the outstanding corrosion resistance -- Element E -- at least -- more than 1at% -- adding is desirable. Moreover, it is more desirable not to add E, in order to attain the high residual magnetization (Ir) of 120 or more emu/g.

[0028] Moreover, in the hard magnetic material of this invention, if it carries out as [contain / in addition to Fe / in T element / Co], the absolute value of the temperature coefficient of the magnetization when using it in a configuration from which a permeance coefficient (p) becomes ten or more especially can be made small. Since the content of Co element results in change to the raw material cost of an alloy, and the magnitude of magnetization, as for the rate of Co element occupied in the whole T element, it is preferably desirable to consider as 20% or less of range 5% or more still more preferably 20% or less 0.5% or more more preferably, and to set up suitably according to a presentation, heat treatment conditions, etc. of an alloy 50% or less.

[0029] Moreover, in the hard magnetic material of this invention, if Si element is added in T element substitute, the absolute value of the temperature coefficient of the magnetization when using it in a configuration from which magnetic properties especially coercive force (iHc), and the maximum magnetic energy product ((BH) max) are further raised, and a permeance coefficient (p) becomes ten or more can be made low. Since the presentation ratio of T element becomes low and the magnetic properties of a hard magnetic material will fall on the contrary if many [too], as for the addition of Si element, it is preferably desirable less than [more than 0.5at%5at%] and to consider as the range not more than more than 0.5at%3at% more preferably, and to set up suitably according to a presentation, heat treatment conditions, etc. of an alloy. Thus, especially the hard magnetic material by which coercive force and the temperature characteristic have been improved is suitably used as the magnet for small motors, and a sensor.

[0030] Next, the hard magnetic material concerning this invention can be manufactured as follows. The method by the melt quenching method, or sputtering and CVD methods, such as the method of spraying and quenching a molten metal to a rotating drum, and forming in thin band-like one and the method of spouting a molten metal in the gas for cooling, quenching in the state of a drop, and forming in the shape of powder, etc. can be used for the method of obtaining the above amorphous alloys. Moreover, when acquiring the consolidation object which can perform heat treatment to the above-mentioned amorphous alloy using the heating means of arbitration, for example, consists of a hard magnetic material of this invention, while making an amorphous alloy into the shape of powder first and carrying out pressing of the end of an alloy powder with a hotpress, the method of heat-treating at a suitable programming rate and heat treatment temperature (annealing temperature) can be used preferably.

[0031] By 10K/, above, the programming rate at the time of heat treatment is the above range by 100K/, and is preferably set up with the presentation of an amorphous alloy. Since the switched connection property of a software magnetism phase (bcc(body-centered cubic structure)-Fe) and a hard magnetism phase (R2Fe14B) falls in order that the crystal grain which deposits in an alloy that the programming rate at the time of heat treatment is the following by 10K/by heat treatment may make it big and rough, and ***** deteriorates, it is not desirable. Moreover, formation of a more uniform detailed organization is attained by making the programming rate at the time of heat treatment into the above range by 100K/. In addition, as a maximum of a programming rate, it may be about a 200K/minute from the constraint on equipment.

[0032] the heat treatment temperature at the time of heat treatment (annealing temperature) -- desirable -- 873K-1173K -- it is more desirable and the range of 973K-1023K and the holding time (heat treatment time amount) are desirable, and it is a range for 3 - 10 minutes more preferably, and is preferably set up with the presentation of an amorphous alloy for 1 to 20 minutes. Since there are few amounts of deposits of the R2Fe14 B phase which bears ***** as heat treatment temperature is less than 873K, sufficient ***** is not obtained, and it is not desirable. On the other hand, if heat treatment temperature exceeds 1173K, since other sludges will deposit, or big and rough-ization of crystal grain will start and ***** will fall, it is not desirable.

[0033] x which a presentation is TxMyRzBw and shows a presentation ratio as the above-mentioned amorphous alloy, and y, z and w use what is satisfied with atomic % of $50 \leq x \leq 60$, $0 \leq y \leq 15$, $3 \leq z \leq 20$, and the

relation it is unrelated $3 \leq w \leq 20$, By using what is more preferably satisfied with atomic % of $86 \leq x \leq 92$, $0.5 \leq y \leq 3$, $3 \leq z \leq 7$, and the relation it is unrelated $3 \leq w \leq 7$. Since the compound which gives ***** from a good amorphous phase being obtained in the state of quenching, and being heat-treated with the above programming rate by 10K/after this deposits even if the concentration of rare earth elements is low, the hard magnetic material which has ***** excellent in low cost can be obtained. Moreover, as the above-mentioned amorphous alloy, a presentation is $T_xM_yR_zB_wE_v$, x which shows a presentation ratio, and y , z , w and v are atomic %s, and it is desirable at the point which can equip also with corrosion resistance the hard magnetic material obtained after heat treatment to use what satisfies $50 \leq x \leq 60$, $0 \leq y \leq 10$, $3 \leq z \leq 15$, $3 \leq w \leq 20$, and the relation it is unrelated $0 \leq v \leq 10$. Moreover, x which shows the presentation ratio in an empirical formula here, and y , z , w and v are atomic %s, and can obtain ***** in which ***** was more excellent by satisfying $80 \leq x \leq 92$, $1 \leq y \leq 5$, $4 \leq z \leq 10$, $3 \leq w \leq 7$, and the relation it is unrelated $0 \leq v \leq 5$.

[0034] Moreover, the absolute value of the temperature coefficient of magnetization when using the thing which did 0.5- pentatomic % addition of Si element in T element substitute, or the thing which included Co in T element in addition to Fe as the above-mentioned amorphous alloy uses the hard magnetic material obtained after heat treatment in the configuration from which a permeance coefficient becomes ten or more is desirable at the point that the following [0.10% / K] can be obtained.

[0035] Thus, if it is in the obtained hard magnetic material By heat-treating the alloy which makes an amorphous phase the main phase immediately after the above-mentioned quenching especially with the above programming rate by 10K/ The difference of the crystallization temperature of R2Fe14 B phase and the crystallization temperature of a bcc-Fe phase is small. Since the inclination which can crystallize simultaneously a bcc-Fe phase and R2Fe14 B phase is strong, it can prevent that one of crystal phases make it big and rough, and the diameter of average crystal grain of the bcc-Fe phase of a fine crystalline phase and R2Fe14 B phase which deposits in the above-mentioned alloy can be made detailed.

Furthermore, from a bcc-Fe phase, since the diameter of average crystal grain is greatly dependent on a programming rate from a bcc-Fe phase a small top, R2Fe14 B phase The probability for the particle of bcc-Fe and the particle of R2Fe14B to adjoin each other by considering the programming rate at the time of heat treatment as the above by 10K/increases. Since the switched connection of a software magnetism phase (bcc(body-centered cubic structure)-Fe) and a hard magnetism phase (R2Fe14B) becomes is easy to be performed, a switched connection property improves. Residual magnetization (I_r), a square shape ratio (I_r/I_s), coercive force (I_{Hc}), and the maximum magnetic energy product ((BH) max) increase, and outstanding ***** is obtained. Specifically, the hard magnetic material which has the residual magnetization beyond 1T (I_r), the hard magnetic material which has the coercive force (I_{Hc}) of 1 or more kOes, and the outstanding hard magnetic material to which 0.6 or more hard magnetic materials and the maximum magnetic energy product ((BH) max) exceed [a square shape ratio (I_r/I_s)] 60 kJ/m³ are realizable.

[0036] Furthermore, since ***** which was excellent even if it lessened the content of rare earth elements R is obtained, the hard magnetic material concerning this invention can be manufactured with a comparatively low manufacturing cost. Moreover, if it is in the hard magnetic material concerning this invention, the absolute value of the temperature coefficient of the magnetization when using Si element in the configuration from which a permeance coefficient becomes ten or more by Co being made to be contained in 0.5 – pentatomic % addition or T element in addition to Fe 0.5 to 20% in T element substitute can realize the following [0.10% / K], and can raise the temperature characteristic. Therefore, the hard magnetic material concerning this invention can be used suitable for sensors, such as a magnetic type rotary encoder and a potentiometer, an actuator, a loudspeaker, a motor, etc.

[0037]

[Example]

(Example 1 of an experiment) It faced heat-treating the quenching thin band alloy of various presentations as follows, the programming rate was changed, and the hard magnetic material was produced. First, the quenching thin band alloy with a thickness of about 20 micrometers was produced by producing an ingot

with an arc solution process and blowing off the metal which dissolved on Cu roll which is rotating in Ar ambient atmosphere from the narrow width nozzle of 0.3mm of slit ***. The density of the obtained quenching thin band alloy was 7.6 g/cm³. Subsequently, it investigated about the effect affect the magnetic properties and the nano crystal structure of a thin band alloy sample which are heat-treated and acquired on the conditions which heat the obtained quenching thin band alloy by part for a programming rate 3 – 216K/all over the infrared image furnace of 1x10 – 2 or less Pa, and are held for about 180 seconds by 973K or 1023K. Fe88Nb2Pr5 B5 which each presentation of the thin band alloy sample obtained here has within the limits of this invention -- the thin band alloy of a presentation, and Fe88Nb2Nd5 B5 -- it was the thin band alloy of a presentation. A result is shown in the following table 1 – a table 4. In addition, Ir/Is is the rate of the residual magnetization to saturation magnetization among a table 1 – a table 4.

[0038] The magnetic properties of the obtained thin band alloy sample were measured at the room temperature all over the impression magnetic field of 15kOe using VSM (oscillating sample mold magnetometer). Although magnetization may not be saturated with the impression magnetic field of 15kOe depending on a sample, in this explanation, it was dealt with as saturation magnetization as what is saturated mostly. Moreover, analysis of the nano crystal structure was performed by calculating the lattice constant of a bcc-Fe phase from an X diffraction peak, and calculating the diameter of average crystal grain of a bcc-Fe phase using the formula of SHIERA from the half peak width of an X diffraction peak.

[0039]

[A table 1]

Fe₈₈Nb₂Pr₅B₅(973K)

サンプルNo.	磁気特性	昇温速度 (K/分)	残留磁化 (T)	Ir/Is	保磁力 k O e	最大磁気工率-積 (kJ/m ³)	格子定数 (nm)	平均結晶粒径 (nm)
1 (実施例)		180	1.46	0.83	2.17	91	0.2871	35
2 (実施例)		102	1.45	0.82	1.79	74	0.2872	36
3 (実施例)		36	1.38	0.78	2.33	82	0.28695	43
4 (実施例)		18	1.39	0.78	1.90	67	0.28719	46
5 (比較例)		6	1.15	0.66	1.99	51	0.28731	48
6 (比較例)		3	1.12	0.64	1.88	48	—	—

[0040]

[A table 2]

Fe₈₈Nb₂Pr₅B₅(1023K)

磁気特性 サンプルNo.	昇温 速度 (K/分)	残留 磁化 (T)	Ir/Is	保磁力 k Oe	最大磁気 エネルギー積 (kJ/m ³)	格子定数 (nm)	平均結晶 粒径 (nm)
7 (実施例)	180	1.37	0.76	2.44	81	0.28727	35.2
8 (実施例)	102	1.28	0.74	1.91	52	0.28727	34.7
9 (実施例)	36	1.33	0.74	2.43	75	0.28707	37.2
10 (実施例)	18	1.26	0.70	1.64	37	0.28714	45.6
11 (比較例)	6	1.15	0.64	1.32	23	0.28711	46
12 (比較例)	3	1.11	0.62	1.26	21	—	—

[0041]

[A table 3]

Fe₈₈Nb₂Nd₅B₅(973K)

磁気特性 サンプルNo.	昇温 速度 (K/分)	残留 磁化 (T)	Ir/Is	保磁力 k Oe	最大磁気 エネルギー積 (kJ/m ³)	格子定数 (nm)	平均結晶 粒径 (nm)
13 (実施例)	180	1.38	0.84	1.86	83	0.2871	27
14 (実施例)	102	1.34	0.81	1.90	81	0.28682	26
15 (実施例)	36	1.32	0.79	1.85	75	0.28705	33
16 (実施例)	18	1.28	0.77	1.54	43	0.28719	42
17 (比較例)	6	1.11	0.66	2.00	57	0.2875	37
18 (比較例)	3	1.05	0.69	1.82	23	—	—

[0042]

[A table 4]

磁気特性 サンプルNo.	昇温 速度 (K/分)	残留 磁化 (T)	Ir/Is	保磁力 kOe	最大磁気 エネルギー積 (kJ/m ³)	格子定数 (nm)	平均結晶 粒径 (nm)
19 (実施例)	180	1.5	0.81	2.46	119	0.2873	28.9
20 (実施例)	102	1.48	0.80	2.37	102	0.28714	32.4
21 (実施例)	36	1.32	0.71	2.05	54	0.28714	37.4
22 (実施例)	18	1.36	0.73	2.21	83	0.28715	29.5
23 (比較例)	6	1.17	0.62	2.16	46	0.2873	35.1
24 (比較例)	3	1.09	0.58	2.01	32	—	—

[0043] Fe88Nb2Pr5 B5 [drawing 2 / drawing 1 –] after heat treatment in 973K–1023K -- the thin band alloy sample of a presentation, and Fe88Nb2Nd5 B5 -- it is drawing showing the lattice constant of the bcc–Fe phase of the thin band alloy sample of a presentation, and the programming rate dependency of the diameter of average crystal grain. Fe88Nb2Pr5 B5 lowered at the same speed as a programming rate after holding drawing 3 – drawing 4 for 5 minutes at the heat treatment temperature of 973K–1023K -- the thin band alloy sample of a presentation, and Fe88Nb2Nd5 B5 -- it is drawing showing the programming rate dependency of the residual magnetization (Ir) of the thin band alloy sample of a presentation, a square shape ratio (Ir/Is), coercive force (iHc), and the maximum magnetic energy product ((BH) max). in order [moreover,] to clarify the diameter of average crystal grain of a bcc–Fe phase, and relation of magnetic properties -- drawing 5 -- Fe88Nb2(Pr, Nd) 5 B5 -- the diameter of average crystal grain of a bcc–Fe phase and the relation of magnetic properties for which it asked from the X diffraction half peak width of the thin band alloy sample of a presentation are shown. Ta is the annealing temperature at the time of heat treatment among drawing 1 – drawing 5 . An alternate long and short dash line shows the relation between the lattice constant of bcc–Fe (pure–Fe), and a programming rate among drawing 1 – drawing 2 for a comparison.

[0044] By making quick the programming rate at the time of heat treatment so that clearly from tables 1–4 and drawing 1 – drawing 2 The programming rate dependency of the lattice constant of the bcc phase of the thin band alloy sample of a presentation is not accepted. Fe88Nb2Pr5 B5 after heat treatment in 973–1023K -- the thin band alloy sample of a presentation, and Fe88Nb2Nd5 B5 -- Although the larger value than pure–Fe with a lattice constant of 0.28665nm is shown, it turns out that the diameter of average crystal grain of a bcc–Fe phase is made detailed with lifting of a programming rate. moreover -- the thin band alloy sample heat–treated with the quickest programming rate (a part for 216K/) -- Fe88Nb2Pr5 B5 – – the thin band alloy sample of a presentation, and Fe88Nb2Nd5 B5 -- in the thin band alloy sample of a presentation, the diameter of crystal grain of a bcc phase became the value of about 35nm and 27–29nm, respectively.

[0045] By making quick the programming rate at the time of heat treatment so that clearly from a table 1 – a table 2, and drawing 3 Fe88Nb2Pr5 B5 after heat treatment of 973K -- with the thin band alloy sample of a presentation Fe88Nb2Pr5 B5 after heat treatment of 1023K -- the increment in Ir and Ir/Is was accepted and both the thin band alloy samples of a presentation of the increasing rate were more remarkable in the thin band alloy sample after heat treatment of 1023K than the thing after heat treatment of 973K. the next -- iHc -- Fe88Nb2Pr5 B5 after heat treatment of 973K -- although a programming rate dependency is not accepted in the thin band alloy sample of a presentation -- Fe88Nb2Pr5 B5 of 1023K -- a programming rate dependency is accepted in the thin band alloy sample of a presentation. Thus, it is thought that that Ir and iHc increase originates in improvement in the switched connection property by the

diameter of average crystal grain of a bcc-Fe phase making it detailed. However, the difference with the programming rate dependency of the diameter of average crystal grain of a bcc-Fe phase clear by the sample after heat treatment and the sample after heat treatment of 1023K is not accepted by 973K, but the thing with the large programming rate dependency of Ir and iHc is imagined to be a thing with factors other than the diameter of crystal grain of a bcc-Fe phase by the sample after heat treatment of 1023K. the next -- (BH) max -- Fe88Nb2Pr5 B5 after heat treatment of 973K -- Fe88Nb2Pr5 B5 after the thin band alloy sample of a presentation, and heat treatment of 1023K -- the programming rate dependency was accepted and both the thin band alloy samples of a presentation of the increasing rate were remarkable in the sample after heat treatment of 1023K.

[0046] making quick the programming rate at the time of heat treatment so that clearly from a table 2 - a table 4, and drawing 4 -- Fe88Nb2Nd5 B5 after heat treatment of 973K -- Fe88Nb2Nd5 B5 after the thin band alloy sample of a presentation, and heat treatment of 1023K -- the increment in Ir and Ir/Is accepts [both the thin band alloy samples of a presentation] -- having -- the increasing rate -- Fe88Nb2Pr5 B5 -- the thin band alloy sample of a presentation was not large. Next about iHc, most programming rate dependencies are not accepted. the next -- (BH) max -- Fe88Nb2Nd5 B5 after heat treatment of 973K -- Fe88Nb2Nd5 B5 after the thin band alloy sample of a presentation, and heat treatment of 1023K -- the programming rate dependency was accepted and both the thin band alloy samples of a presentation of the increasing rate were remarkable in the sample after heat treatment of 1023K. Fe88Nb2Nd5 B5 -- the programming rate dependency of magnetic properties, such as Ir of the thin band alloy sample of a presentation, and iHc, -- Fe88Nb2Pr5 B5 -- it is considered to be what has the small effect that the diameter of crystal grain of a bcc phase originates in the particle size of a bcc-Fe phase since it is detailed on the whole that is not so clear as the thin band alloy sample of a presentation. moreover, as for residual magnetization (Ir), by 1.26T (sample No.10) and the largest thing, the big value of 1.5T (sample No.19) is acquired also for the smallest thing among the example of a table 1 - a table 4. That is, when it converts from the density of each sample being 7.6 g/cm³, it turns out that it becomes 131 emu/g - 157 emu/g, and the big residual magnetization of 130 or more emu/g is obtained.

[0047] clear from drawing 5 -- as -- Fe88Nb2Pr5 B5 -- the thin band alloy sample of a presentation, and Fe88Nb2Nd5 B5 -- it turns out that the diameter of crystal grain of a bcc-Fe phase follows the thin band alloy sample of a presentation on increasing, and there is an inclination for Ir/Is, iHc, and (BH) max to decrease.

[0048] The presentation was the range of this invention, it heated with the quick programming rate and the above-mentioned experimental result showed that the structure in which the fine crystalline phase of ***** with the high thin band alloy sample heat-treated and obtained by 973K-1023K and 100nm or less of diameters of average crystal grain deposited was acquired. Moreover, since the diameter of average crystal grain of a bcc-Fe phase became [the programming rate] small above by 10K/and ***** such as Ir/Is, iHc, and (BH) max, were excellent, in this invention, the programming rate at the time of heat treatment was considered as the above by 10K/. Moreover, in order to acquire higher magnetic properties, it turned out more preferably that it is good to consider a programming rate as a part for 36K/. In the thin band alloy sample of a presentation further -- a programming rate -- a part for 100K/ -- the above -- Fe88Nb2Pr5 B5 -- the thin band alloy sample of a presentation, and Fe88Nb2Nd5 B5 -- The diameter of crystal grain of a bcc-Fe phase, respectively About 35-36nm and about 26-32.5nm, It was made detailed more, and since especially coercive force was excellent with about 1.8 to 2.45 kOe, and about 1.85 to 2.45 kOe, respectively, it considered preferably the programming rate at the time of heat treatment as the above by 100K/in this invention.

[0049] (Example 2 of an experiment) It faced heat-treating a quenching thin band alloy as follows, the holding time was changed, and the hard magnetic material was produced. The quenching thin band alloy with a thickness of about 20 micrometers was produced like the above-mentioned example 1 of an experiment, and this quenching thin band alloy was further cut into a length of 2cm. Subsequently, it investigated about the effect affect the magnetic properties of the thin band alloy sample heat-treated and obtained on the conditions which heat a quenching thin band alloy with a length of 2cm by part for

programming rate 18K/all over the infrared image furnace of about 20 and $1 \times 10 - 5$ Pa or less, and are held for [3 minutes -] 60 minutes at the heat treatment temperature (annealing temperature) 973K-1073K. Each presentation of the thin band alloy sample obtained here was a presentation which is within the limits of this invention and which becomes Fe84Nb2Nd7 B5Si2. A result is shown following table 5. Moreover, the heat treatment time amount (holding time) dependency of the magnetic properties of the thin band alloy sample of the presentation which becomes drawing 6 Fe84Nb2Nd7 B5Si2 is shown. Moreover, each heat treatment conditions show the heat treatment time amount (holding time) dependency of the X-ray pattern of the thin band alloy sample of the presentation which becomes Fe84Nb2Nd7 B5Si2 after heat treatment to drawing 7 - drawing 9. The X diffraction pattern of a thin band alloy sample here was analyzed by the X-ray diffractometer which used Cu-K alpha rays.

[0050]

[A table 5]

熱処理温度 (K)	保持時間3分の ときの iHc(kOe)	保持時間10分の ときの iHc(kOe)	保持時間30分の ときの iHc(kOe)	保持時間60分の ときの iHc(kOe)
973	0. 48	1. 56	3. 2	3. 36
1023	3. 44	3. 5	3. 09	2. 89
1073	2. 93	2. 78	2. 6	2. 51

[0051] clear from a table 5 and drawing 6 -- as -- a part for programming rate 18K/--- Fe -- when a 84Nb2Nd7 B5Si2 quenching thin band alloy (2cmx20**) was heat-treated, as for conditions when coercive force becomes max (3.5kOe), it turned out that heat treatment temperature is holding-time 10 minutes in 1023K. Moreover, it turned out that holding-time 60 minutes, and heat treatment temperature are acquired by 973K, and heat treatment temperature is acquired for the good ***** of coercive force abbreviation 3.38kOe by 1023K at the time of the conditions for holding-time 3 minutes. Moreover, heat treatment temperature was [the coercive force of heat treatment by 1073K] 3 or less kOes in all the holding times.

[0052] Since Fe3B which does not contribute to ***** when the holding times are 3 minutes - 30 minutes and short conditions after heat treatment Fe84Nb2Nd7 B5Si2 deposits by part for programming rate 18K/, and annealing temperature 973K so that clearly from drawing 7 , and Nd2Fe14B which shows ***** hardly deposits, the X diffraction pattern of the sample of the becoming presentation is understood that coercive force is not high as shown in a table 5 and drawing 6 . On the other hand, when the holding times are 60 minutes and long conditions, Nd2Fe14B deposits, the heat treatment temperature a sample indicates good magnetic properties to be is fully reached, and it turns out that high coercive force is acquired. As for the X diffraction pattern of the sample of the presentation which becomes Fe84Nb2Nd7 B5Si2 after heat treatment, it is admitted by part for programming rate 18K/, and annealing temperature 1023K that Nd2Fe14B deposits by all the holding times so that clearly from drawing 8 . It is thought that it is because the crystal grain of a software magnetism phase (bcc-Fe phase) carried out grain growth when ***** will decrease if ***** is high as it was shown in a table 5 and drawing 6 , when the holding times were 3 minutes and 10 minutes especially, and the holding time becomes as long as 30 minutes and 60 minutes to this, that reason has reached the optimal heat treatment temperature enough in [holding-time] 3 - 10 minutes and it heat-treated further after this. It is thought that it is because the crystal grain of a software magnetism phase (bcc-Fe phase) carried out grain growth of whose ***** having not been so high as the X diffraction pattern of the sample of the presentation which it becomes after heat treatment Fe84Nb2Nd7 B5Si2 by part for programming rate 18K/and annealing temperature 1073K so that clearly from drawing 9 was shown in a table 5 and drawing 6 , although the deposit of Nd2Fe14B was accepted by all the holding times since the heat treatment temperature itself became high

too much.

[0053] (Example 3 of an experiment) It faced heat-treating a quenching thin band alloy as follows, the amount of heat treatments (input of a quenching thin band alloy) was changed, and the hard magnetic material was produced. The quenching thin band alloy with a thickness of about 20 micrometers was produced like the above-mentioned example 1 of an experiment. Subsequently, 20 quenching thin band alloys (AUW of about 20mg) and four 2.5g quenching thin band alloys (AUW of 10g) which were cut into a length of 2cm are set all over the infrared image furnace of 1x10 - 5 or less Pa, respectively. The heat treatment conditions from which good ***** understood in the above-mentioned example 2 of an experiment is obtained (** heat treatment temperature is 973K by the 60 holding time) ** Heat treatment temperature investigated about the effect the amount of heat treatments of the thin band alloy sample which ** heat treatment temperature heat-treats all programming rates by part for 18K/in the heat treatment conditions of *** - ** for holding-time 10 minutes for holding-time 3 minutes by 1023K, and is obtained by 1023K affects coercive force. The presentation of the thin band alloy sample obtained here was a becoming presentation Fe84Nb2Nd7 B5Si2. A result is shown following table 6.

[0054]

[A table 6]

熱処理量 (投入量)	973K-保持時間60分 のときの iHc(kOe)	1023K-保持時間3分 のときの iHc(kOe)	1023K-保持時間10分 のときの iHc(kOe)
2 cm × 20 本	3. 3 6	3. 4 4	3. 5
2. 5 g × 4 個	3. 7 3	3. 3 3	3. 4 9

[0055] So that clearly from a table 6 an increase and the sample of Fe84Nb2Nd7 B5Si2 heat-treated and obtained on the heat treatment conditions of the above-mentioned ** - ** even if carried out the input of a quenching thin band alloy since it has high coercive force, it is high coercive force -- etc. -- as suitable heat treatment conditions for manufacturing the hard magnetic material excellent in ***** When the presentation of a hard magnetic material is Fe84Nb2Nd7 B5Si2, it is a part for ** programming rate 18K/. And it turned out that it is a part for maintenance and ** programming rate 18K/for 60 minutes in heat treatment temperature 973K, is a part for maintenance and ** programming rate 18K/for 3 minutes in heat treatment temperature 1023K, and is maintenance for 10 minutes in heat treatment temperature 1023K.

[0056] (Example 4 of an experiment) Fe88Nb2Pr5 B5 -- the amorphous alloy thin band after quenching of a presentation was heated by part for programming rate 180K/, and the temperature change of magnetization of the hard magnetic material heat-treated and obtained with the annealing temperature of 750 degrees C was investigated. moreover, Fe88Pr7 B5 -- the amorphous alloy thin band after quenching of a presentation was heated by part for programming rate 180K/, and the temperature change of magnetization of the hard magnetic material heat-treated and obtained with the annealing temperature of 650 degrees C was investigated. The result is shown in drawing 10 . drawing 10 -- Fe88Nb2Pr5 B5 -- the hard magnetic material of a presentation, and Fe88Pr7 B5 -- it is drawing showing the temperature change of magnetization of the hard magnetic material of a presentation. Magnetization is decreasing at two steps with lifting of temperature as shown in drawing 10 . It is admitted that two phases of phases which participate in magnetization of a hard magnetic material exist from this. Moreover, since the degree of reduction in magnetization is changing near 307 degree C, this neighborhood is the Curie temperature of a Fe14Nd2B phase, and since the degree of reduction in magnetization is changing near 800 degree C, it turns out that this neighborhood is the Curie temperature of a bcc-Fe phase. In addition, it is considered to be because for a volume fraction to be [that magnetization is low and] small that the step of the magnetization which originates in an amorphous phase here is not seen.

[0057] moreover, Fe88Nb2Pr5 B5 obtained here -- the hard magnetic material of a presentation, and Fe88Pr7 B5 -- the 2nd quadrant of the magnetization curve of the hard magnetic material of a

presentation is shown in drawing 11. The magnetization curve is the same magnetization curve as the magnetic material which consists of a single phase as which a step is not regarded as shown in drawing 11, and it turns out that the switched connection magnet which the detailed software magnetism phase and the hard magnetism phase combined magnetically is obtained.

[0058] (Example 5 of an experiment) The quenching thin band alloy of various presentations was produced like the above-mentioned example 1 of an experiment. Subsequently, the obtained quenching thin band alloy was heated by part for programming rate 180K/all over the infrared image furnace of $1 \times 10 - 2$ or less Pa, it heat-treated on the conditions held for about 3 minutes by annealing temperature 1023K, and the thin band alloy sample (example) was obtained. Fe88Nb2Pr5 B5 which each presentation of the thin band alloy sample obtained here has within the limits of this invention -- the thin band alloy of a presentation, and Fe76Co10Nb2Pr7 B5 -- the thin band alloy of a presentation, and Fe66Co20Nb2Pr7 B5 -- the thin band alloy of a presentation, and Fe84Nb2Pr7 B5Si2 -- it was the thin band alloy of a presentation. the thin band alloy sample of the acquired example -- VSM (oscillating sample mold magnetometer) -- using -- the inside of the impression magnetic field of 10kOe, and a vacuum -- room temperature -- about 490 -- the demagnetization curve (the 2nd quadrant) in K is shown in drawing 12 -- drawing 14. I is a straight line whose permeance coefficient (p) is 10 (prism form) among drawing 13, and RO is a straight line whose p is 1.5 (disc form). Moreover, the residual magnetization (Ir) for which it asked from the demagnetization curve (the 2nd quadrant), and the temperature change of coercive force (iHc) were shown in drawing 15 about the relation between the magnetic properties of the thin band alloy sample of an example, and temperature. Moreover, the temperature coefficient of Ir and iHc of the obtained thin band alloy sample and the temperature coefficient of Ir when considering as p= 1.5 and the configuration used as p= 10 are shown in a table 7.

[0059] The relation between the magnetic properties of the conventional ferrite magnet and a Nd-Fe-B system magnet and temperature is shown according to drawing 15 as an example of a comparison. The temperature coefficient of Ir and iHc of these conventional magnets is shown according to a table 7. moreover -- as the example of a comparison -- B -- the temperature coefficient of Ir and iHc of the magnet of a rich Nd-Fe-B system is shown in a table 8.

[0060]

[A table 7]

Ir及びiHcの温度係数 (室温~約490K)

	硬磁性材料の組成	dIr/dT (%/K)	diHc/dT (%/K)	P=1.5のときの dI/dT(%/K)	P=10のときの dI/dT(%/K)
実 施 例	Fe88Nb2Pr5B5 Fe76Co10Nb2Pr7B5 Fe66Co20Nb2Pr7B5 Fe84Nb2Pr7B5Si2	-0. 06 -0. 02 -0. 02 -0. 02	-0. 43 -0. 28 -0. 36 -0. 32	-0. 38 -0. 20 -0. 33 -0. 17	-0. 12 -0. 10 -0. 08 -0. 05
比 較 例	Fe77Nd15B6 (Fe0.8Co0.1)77Nd15B6 フェライト磁石	0. 16 -0. 11 -0. 18	0. 4 -0. 35 --	-- -- --	-- -- --

[0061]

[A table 8]

	硬磁性材料の組成	dIr/dT (%/K)	diHc/dT (%/K)	温度範囲 (K)
比 較 例	$Nd_5Fe_{78.5}B_{18.5}$	-0. 0 4 3	-0. 3 9 8	2 9 7 - 4 1 3
	$Nd_5Fe_{70.5}Co_5Ga_3B_{18.5}$	-0. 0 7 4	-0. 3 3 6	2 9 7 - 4 1 3
	$Nd_3Dy_2Fe_{70.5}Co_5Ga_1B_{18.5}$	-0. 0 4 8	-0. 3 6 1	2 9 7 - 4 1 3
	$Nd_{3.5}Dy_1Fe_{73}Co_3Ga_1B_{18.5}$	-0. 0 8	-0. 3 9	3 4 8 付近

[0062] As for the magnet of the thin band alloy sample of an example, and the example of a comparison, the inclination for Ir and iHc to decrease with lifting of temperature is accepted from drawing 15 and a table 7: the temperature coefficient (diHc/dT) of iHc — Fe88Nb2Pr5 B5 of an example — although the samples of a presentation are -0.43%/K and are the values near the value (-0.4%/K) of the Nd-Fe-B system magnet of the example of a comparison, by the thin band alloy sample of the example which added Co and Si, being a value with the absolute value of a temperature coefficient smaller than the Nd-Fe-B system magnet of -0.28 -- -0.36% / K, and the example of a comparison is admitted. Thus, it is considered to originate in the Curie temperature of a hard magnetism phase rising by adding Co that the absolute value of the temperature coefficient of iHc decreases. Moreover, if Si is added, in order to improve the whole coercive force, the absolute value of the temperature coefficient of iHc decreases as a result.

[0063] next — the temperature coefficient (dIr/dT) of Ir — Fe88Nb2Pr5 B5 of an example — the samples of a presentation are -0.06%/K, and it is admitted that the absolute value of a temperature coefficient is low compared with the values of the Nd-Fe-B system magnet (Fe77 Nd five B8 the magnet of a presentation, 77 (Fe0.9Co0.1) Nd 15B8 magnet of a presentation) of the example of a comparison being -0.11 -- -0.16%/K. the phase to which this participates in magnetization with the magnet of the example of a comparison — a hard magnetism phase — it is — it receives and it is thought by the thin band alloy sample of an example that it is because it has the nano diplophase organization where the hard magnetism phase and the software magnetism phase with the small rate of a temperature change of magnetization (bcc-Fe phase) were intermingled. Moreover, by the thin band alloy sample of the example which added Co and Si, the temperature coefficients of Ir are -0.02%/K, and it is admitted that the absolute value of a temperature coefficient is a substantially small value. the temperature coefficient of Ir and iHc of the thin band alloy sample of a table 7 and a table 8 to an example — B — being the same degree as the temperature coefficient of Ir and iHc of the magnet of a rich Nd-Fe-B system or a value not more than it are admitted. drawing 13 to Fe66Co20Nb2Pr7 B5 — the sample of a presentation has the small temperature change of magnetization in p= 10 or more fields, and it turns out that the temperature characteristic is excellent.

[0064] It asks for drawing 16 from the demagnetization curve which showed the value of Ir in each temperature when using the thin band alloy sample of an example in the configuration used as p= 10 to drawing 12 – drawing 14 . Moreover, the temperature change of Ir when using a conventional Sm-Co magnet and a conventional Nd-Fe-B system magnet (Nd2Fe14B presentation) in the configuration used as p= 10 is shown according to drawing 16 for a comparison. Fe88Nb2Nd5 B5 which drawing 17 has within the limits of the presentation of this invention — the sintering bulk (alloy consolidation object) sample of a presentation, and Fe86Nb2Pr7 B5 — the relation between the permeance coefficient of the thin band alloy sample of a presentation and a temperature coefficient is shown. Moreover, the relation between the permeance coefficient of the conventional Nd-Fe-B system magnet (Nd2Fe14B presentation) and a temperature coefficient is shown according to drawing 17 for a comparison.

[0065] the time of using it in the configuration set to p= 10 from a table 7 and drawing 16 – drawing 17 — Fe88Nb2Nd5 B5 of an example, although temperature coefficients are -0.12%/K and the sample of a presentation is the same degree as the temperature coefficient of the conventional Nd-Fe-B system magnet Fe84Nb2Pr7 B5Si2 of the example which added Si — Fe66Co20Nb2Pr7 B5 of the example which

the samples of a presentation are $-0.05\%/\text{K}$, and added Co -- it turns out that the sample of a presentation shows the value with the small absolute value of $-0.08\%/\text{K}$, and a temperature coefficient. Moreover, when it is used in the configuration used as $p=10$, it turns out that the thin band alloy sample of an example and especially the sample of the presentation which becomes Fe84Nb2Pr7 B5Si2 have the small absolute value of a temperature coefficient in about $300\text{--}430\text{K}$ operating temperature range, and it has the temperature characteristic which was excellent in the same degree as the Sm-Co system magnet of the example of a comparison, and the temperature characteristic is superior to the Nd-Fe-B system magnet of the example of a comparison. When a permeance coefficient uses the sample of an example or more by ten from drawing 17, the absolute value of a temperature coefficient is smaller than the Nd-Fe-B system magnet of the example of a comparison, and it turns out that the temperature characteristic is excellent.

[0066] (Example 6 of an experiment) It investigated about the effect affect the magnetic properties and the nano crystal structure of a thin band alloy sample which are heat-treated and acquired on the conditions which heat the quenching thin band alloy produced like the example 1 of an experiment by part for a programming rate (α) $3\text{--}180\text{K}/\text{all}$ over an infrared image furnace 1.3×10 to 3 torrs or less, and are held for about 180 seconds by $973\text{K}\text{--}1023\text{K}$. Fe88Nb2Nd5 B5 which the presentation of the thin band alloy sample obtained here has within the limits of this invention -- it was the thin band alloy of a presentation. The X-ray diffractometer and the superresolution mold transmission electron microscope (TEM) investigated the structure of the obtained thin band alloy sample, and magnetic properties were searched for by applying the impression magnetic field of 1.5T to the longitudinal direction of a thin band alloy sample at a room temperature using VSM (oscillating sample mold magnetization measuring device).

[0067] Fe(furnace cooling was carried out all over infrared image furnace) 88Nb2Nd5 B5 which quenched after holding drawing 18 for 180 seconds at the heat treatment temperature of 1023K -- it is the graph which shows the programming rate dependency of the demagnetization curve (the 2nd quadrant) of the thin band alloy sample of a presentation. Since, as for the thing of the example which is a part for a part for $180\text{K}/$ which has speed within the limits of this invention whenever [temperature-up] so that clearly from drawing 18, and $18\text{K}/$, it is admitted that I and H are large compared with the thing (a programming rate is a part for $3\text{K}/$) of the example of a comparison, the thing of an example understands that $(BH)_{\text{max}}$ is also large. Fe(furnace cooling was carried out all over infrared image furnace) 88Nb2Nd5 B5 which quenched after holding drawing 19 for 180 seconds at the heat treatment temperature of 1023K -- it is drawing showing the programming rate dependency of I_r of the thin band alloy sample of a presentation, I_r/I_s , iH_c , and $(BH)_{\text{max}}$ clear from drawing 19 -- as -- Fe88Nb2Nd5 B5 -- when the thin band alloy sample of a presentation makes quick the programming rate at the time of heat treatment, it is admitted that I_r , I_r/I_s , iH_c , and $(BH)_{\text{max}}$ are increasing notably. therefore, Fe88Nb2Nd5 B5 which quenched after holding for 180 seconds at the heat treatment temperature of 1023K -- a programming rate dependency is accepted also in the thin band alloy sample of a presentation. Fe(furnace cooling was carried out all over infrared image furnace) 88Nb2Nd5 B5 which drawing 20 made the programming rate at the time of heat treatment as a part for $3\text{--}180\text{K}/$, made the holding time 180 seconds, and quenched after that -- it is drawing showing the heat treatment temperature (retention temperature) dependency of I_r of the thin band alloy sample of a presentation, I_r/I_s , and iH_c . The property with it better [to heat-treat each **** alloy sample with the retention temperature of 1020K] is acquired so that clearly from drawing 20, and it turns out that the magnetic properties in which especially the thing of the example which the programming rate heat-treated by part for $180\text{K}/$, and retention temperature heat-treated by $970\text{--}1070\text{K}$ was excellent compared with the thing of the example of a comparison whose programming rate is a part for $3\text{K}/$ are acquired.

[0068] every which a part for $3\text{--}180\text{K}/$ and retention temperature were made to 1023K , it made the holding time 180 seconds for the programming rate at the time of heat treatment, quenched drawing 21 after that, and was obtained -- Fe88Nb2Nd5 B5 -- it is drawing showing the temperature change of magnetization of the thin band alloy sample of a presentation. It turns out that the temperature change of magnetization of each **** alloy sample from which the programming rate at the time of heat treatment differs so that clearly from drawing 21 is decreasing almost similarly with lifting of temperature. This has

suggested that magnetization is hardly dependent on the programming rate at the time of heat treatment. Fe88Nb2Nd5 B5 which drawing 22 made retention temperature at the time of heat treatment to 1023K, made the holding time 180 seconds, and quenched after that — it is drawing showing the programming rate dependency of the diameter of average crystal grain of the bcc-Fe phase of the thin band alloy sample of a presentation, and Nd2Fe14 B phase. bcc-Fe (TEM) in drawing 22 and Nd2Fe14B (TEM) are the particle size for which it asked from the TEM photograph, respectively, and bcc-Fe (XRD) is the particle size for which it asked from the graph of an X diffraction. What has a small diameter of average crystal grain is obtained as the bcc-Fe phase of a thin band alloy sample and Nd2Fe14 B phase make a programming rate quick so that clearly from drawing 22, and especially as for Nd2Fe14 B phase, a bcc-Fe phase shows depending greatly at a programming rate the top where the diameter of average crystal grain is smaller than a bcc-Fe phase. therefore, Fe88Nb2Nd5 B5 — it turns out that the programming rate dependency of the magnetic properties of the thin band alloy sample of a presentation originates in detailed-ization of the diameter of crystal grain. That is because the switched connection of a software magnetism phase (bcc-Fe) and a hard magnetism phase (Nd2Fe14B) becomes the probability, i.e., the portion which the particle of bcc-Fe and the particle of Nd2Fe14B have combined, for the particle of bcc-Fe and the particle of Nd2Fe14B to adjoin each other increases, and is easy to be performed, so a switched connection property will improve if the diameter of average crystal grain of Nd2Fe14 B phase becomes small.

[0069] Fe88Nb2Nd5 B5 from which drawing 23 was obtained by the melt quenching method — it is drawing showing the DSC (differential scanning calorimetry) curve in each programming rate of the amorphous alloy thin band sample of a presentation. The portion which the first peak in each DSC curve begins is the crystallization temperature (Tx1) of a bcc-Fe phase among drawing 23, and the portion which the 2nd peak begins is the crystallization temperature (Tx2) of Nd2Fe14 B phase. Drawing 24 (a) shows Tx2 of the Tx1 and the Nd2Fe14 B phase of the bcc-Fe phase of the DSC curve in each programming rate shown in drawing 23, and (b) shows the difference of Tx1 of Tx2 and the bcc-Fe phase of the Nd2Fe14 B phase of a DSC curve in each programming rate shown in drawing 23 ($DTx=Tx2-Tx1$). Since the difference (DTx) of Tx1 of Tx2 and the bcc-Fe phase of Nd2Fe14 B phase is small as the programming rate at the time of heat treatment is made quick so that more clearly than drawing 22 – drawing 24, the more DTx is small, the more it turns out that the diameter of average crystal grain of the both sides of a bcc-Fe phase and Nd2Fe14 B phase can be made detailed. That is because the inclination which can crystallize simultaneously a bcc-Fe phase and Nd2Fe14 B phase becomes strong, so one of crystals can prevent making it big and rough, so that DTx becomes small.

[0070]

[Effect of the Invention] As explained above, the hard magnetic material concerning this invention The element R which consists or more of one or more sorts of Elements T and rare earth elements of Fe, Co, and the nickel By coming to heat-treat the alloy which makes an amorphous phase the main phase immediately after quenching with the above programming rate by 10K/including B, since coercive force is 1 or more kOes The diameter of average crystal grain of the bcc-Fe phase of a fine crystalline phase and R2Fe14 B phase which deposits in the above-mentioned alloy can be made detailed. Furthermore, from a bcc-Fe phase, since the diameter of average crystal grain is greatly dependent on a programming rate from a bcc-Fe phase a small top, R2Fe14 B phase The probability for the particle of bcc-Fe and the particle of R2Fe14B to adjoin each other by considering the programming rate at the time of heat treatment as the above by 10K/increases. Since the switched connection of a software magnetism phase (bcc(body-centered cubic structure)-Fe) and a hard magnetism phase (R2Fe14B) becomes is easy to be performed, a switched connection property improves, and outstanding ***** is obtained. Furthermore, since good ***** is obtained even if it lessens the content of rare earth elements R, the hard magnetic material concerning this invention can be manufactured with a comparatively low manufacturing cost.

[0071] It comes to heat-treat the alloy with which the hard magnetic material concerning this invention makes an amorphous phase the main phase immediately after quenching with the above programming rate by 10K/. Since the coercive force which comes to contain the software magnetism phase of 1 or less kOe of coercive force and the hard magnetism phase of 1 or more kOes of coercive force more than

10vol(s)(volume) %, respectively is 1 or more kOes It can have the middle property of a software magnetism phase and a hard magnetism phase, and the absolute value of the temperature coefficient of magnetization can also be made small. It comes to heat-treat the alloy with which the hard magnetic material concerning this invention makes an amorphous phase the main phase immediately after quenching with the above programming rate by 10K/. Since the coercive force in which the magnetic phase and Curie temperature of 600 degrees C or more come for Curie temperature to contain the magnetic phase of 600 degrees C or less more than 10vol(s)(volume) %, respectively is 1 or more kOes It can have the middle property of a software magnetism phase and a hard magnetism phase, and the absolute value of the temperature coefficient of magnetization can also be made small.

[0072] If it is in some which contain the fine crystalline phase of 100nm or less of diameters of average crystal grain as a main phase, the switched connection property of a software magnetism phase and a hard magnetism phase is excellent in the hard magnetic material obtained after heat treatment with the above programming rate by 10K/in the alloy which makes an amorphous phase the main phase immediately after the above-mentioned quenching, and ***** is excellent in it. if it is in the thing which comes to heat-treat the alloy which makes an amorphous phase the main phase immediately after the above-mentioned quenching with the above programming rate by 100K/in the hard magnetic material concerning this invention -- the diameter of average crystal grain -- being small (uniform detailed organization) -- it is realizable. In the hard magnetic material concerning this invention, if the absolute value of the temperature coefficient of the magnetization when using it in the configuration from which a permeance coefficient becomes ten or more especially is one of those which were made into below 0.10% / K, it can be used for products, such as a sensor for which a temperature change needs a small thing.

[0073] According to the hard magnetic material concerning this invention, coercive force can realize the hard magnetic material of 2 or more kOes. Moreover, according to the hard magnetic material concerning this invention, 0.6 or more hard magnetic materials can be realized comparatively (Ir/Is), therefore high residual magnetization (Ir) can be realized, and the hard magnetic material with the high maximum magnetic energy product ((BH) max) of the residual magnetization (Ir) to saturation magnetization (Is) can be obtained. If it is in the hard magnetic material of this invention, x which sets a presentation to TxMyRzBw and shows a presentation ratio, and y, z and w are atomic %. When $50 \leq x \leq 100$, $0 \leq y \leq 15$, $3 \leq z \leq 20$, and the relation it is unrelated $3 \leq w \leq 20$ shall be satisfied and residual magnetization (Ir) considers as the thing of 100 or more emu/g Since the compound which gives ***** from a good amorphous phase being obtained in the state of quenching, and being heat-treated with the above programming rate by subsequent 10K/deposits even if the concentration of rare earth elements is low, the hard magnetic material which has ***** excellent in low cost is obtained. x which shows the presentation ratio in an empirical formula here, and y, z and w can obtain more excellent ***** by satisfying $86 \leq x \leq 92$, $0.5 \leq y \leq 3$, $3 \leq z \leq 7$, and the relation it is unrelated $3 \leq w \leq 7$.

[0074] If it is in the hard magnetic material of this invention, it can also have corrosion resistance further by setting a presentation to TxMyRzBwEv, and x which shows a presentation ratio, and y, z, w and v being atomic %s, and satisfying $50 \leq x \leq 100$, $0 \leq y \leq 10$, $3 \leq z \leq 15$, $3 \leq w \leq 20$, and the relation it is unrelated $0 \leq v \leq 10$. x which shows the presentation ratio in an empirical formula here, and y, z, w and v are atomic %s, and can obtain more excellent ***** by satisfying $80 \leq x \leq 92$, $1 \leq y \leq 5$, $4 \leq z \leq 10$, $3 \leq w \leq 7$, and the relation it is unrelated $0 \leq v \leq 5$. In the hard magnetic material concerning this invention, that 0.5- pentatomic % addition of Si element is done in T element substitute, or by containing Co in T element in addition to Fe, the absolute value of the temperature coefficient of the magnetization when using it in the configuration from which a permeance coefficient becomes ten or more can obtain the following [0.10% / K], and can raise the temperature characteristic. Therefore, if it is in the hard magnetic material of this invention, it is useful as a magnet material used for various kinds of equipments, such as sensors, such as a magnetic type rotary encoder and a potentiometer, an actuator, a loudspeaker, and a motor, and reduction of a manufacturing cost can be aimed at.

[0075] If it is in the manufacture method of the hard magnetic material of this invention, among Fe, Co, and nickel One or more sorts of elements T By having the process which heat-treats this alloy with the above

programming rate by 10K/, after producing the alloy which makes an amorphous phase the main phase with a melt quenching method including the elements R and B which consist of one or more sorts in rare earth elements. The difference of the crystallization temperature of R₂Fe₁₄B phase and the crystallization temperature of a bcc-Fe phase becomes small. Since the inclination which can crystallize simultaneously a bcc-Fe phase and Nd₂Fe₁₄B phase becomes strong, it can prevent that one of crystal phases make it big and rough, and the diameter of average crystal grain of the bcc-Fe phase of a fine crystalline phase and R₂Fe₁₄B phase which deposits in the above-mentioned alloy can be made detailed. Furthermore, from a bcc-Fe phase, since the diameter of average crystal grain is greatly dependent on a programming rate from a bcc-Fe phase a small top, R₂Fe₁₄B phase. The probability for the particle of bcc-Fe and the particle of R₂Fe₁₄B to adjoin each other by considering the programming rate at the time of heat treatment as the above by 10K/increases. Since the switched connection of a software magnetism phase (bcc(body-centered cubic structure)-Fe) and a hard magnetism phase (R₂Fe₁₄B) becomes is easy to be performed, a switched connection property can improve, and the hard magnetic material excellent in ***** can be offered. Moreover, since ***** which was excellent even if it made the content of rare earth elements fewer than the conventional rare earth magnet is obtained, the hard magnetic material of high performance can be manufactured with a comparatively low manufacturing cost.

[0076] Furthermore, if it is in the manufacture method of the hard magnetic material concerning this invention, by heat-treating the alloy which makes the above-mentioned amorphous phase the main phase especially with the above programming rate by 100K/, (BH) max is large and the hard magnetic material in which the uniform fine crystal deposited can be obtained suitably. Moreover, if it is in the manufacture method of the hard magnetic material concerning this invention, it can use suitably as a way the absolute value of the temperature coefficient of the magnetization when using it in the configuration from which a permeance coefficient becomes ten or more obtains the hard magnetic material below 0.10% / K, by using the alloy which did 0.5- pentatomic % addition of Si in T element substitute for the alloy which makes the above-mentioned amorphous phase the main phase especially.

[Translation done.]

* NOTICES *

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Fe88Nb2Pr5 B5 after heat treatment in 973K-1023K -- it is drawing showing the lattice constant of the bcc-Fe phase of the sample of a presentation, and the programming rate dependency of the diameter of average crystal grain.

[Drawing 2] Fe88Nb2Nd5 B5 after heat treatment in 973K-1023K -- it is drawing showing the lattice constant of the bcc-Fe phase of the sample of a presentation, and the programming rate dependency of the diameter of average crystal grain.

[Drawing 3] Fe88Nb2Pr5 B5 lowered at the same speed as a programming rate after holding for 5 minutes at the heat treatment temperature of 973K-1023K -- it is drawing showing the programming rate dependency of the magnetic properties of the sample of a presentation.

[Drawing 4] Fe88Nb2Nd5 B5 lowered at the same speed as a programming rate after holding for 5 minutes at the heat treatment temperature of 973K-1023K -- it is drawing showing the programming rate dependency of the magnetic properties of the sample of a presentation.

[Drawing 5] Fe88Nb2(Pr, Nd) 5 B5 -- it is drawing showing the diameter of average crystal grain of the bcc-Fe phase of the sample of a presentation, and the relation of magnetic properties.

[Drawing 6] It is drawing showing the heat treatment time amount (holding time) dependency of the magnetic properties of the sample of the becoming presentation Fe84Nb2Nd7 B5Si2.

[Drawing 7] They are a part for programming rate 18K/, and drawing showing the heat treatment time amount (holding time) dependency of the X-ray pattern of the sample of the presentation after heat treatment which becomes Fe84Nb2Nd7 B5Si2 by annealing temperature 973K.

[Drawing 8] They are a part for programming rate 18K/, and drawing showing the heat treatment time amount (holding time) dependency of the X-ray pattern of the sample of the presentation after heat treatment which becomes Fe84Nb2Nd7 B5Si2 by annealing temperature 1023K.

[Drawing 9] They are a part for programming rate 18K/, and drawing showing the heat treatment time amount (holding time) dependency of the X-ray pattern of the sample of the presentation after heat treatment which becomes Fe84Nb2Nd7 B5Si2 by annealing temperature 1073K.

[Drawing 10] Fe88Nb2Pr5 B5 -- the hard magnetic material of a presentation, and Fe88Pr7 B5 -- it is the graph which shows the temperature change of magnetization of the hard magnetic material of a presentation.

[Drawing 11] Fe88Nb2Pr5 B5 -- the hard magnetic material of a presentation, and Fe88Pr7 B5 -- it is the 2nd quadrant **** graph of the magnetization curve of the hard magnetic material of a presentation.

[Drawing 12] Fe76Co10Nb2Pr7 B5 -- it is the graph which shows the demagnetization curve (the 2nd quadrant) in 302.5K-489K of the thin band alloy sample of a presentation.

[Drawing 13] Fe66Co20Nb2Pr7 B5 -- it is the graph which shows the demagnetization curve (the 2nd quadrant) in 308K-471K of the thin band alloy sample of a presentation.

[Drawing 14] It is the graph which shows the demagnetization curve (the 2nd quadrant) in 301.5K-477K of the thin band alloy sample of the becoming presentation Fe84Nb2Pr7 B5Si2.

[Drawing 15] It is drawing showing the relation between the magnetic properties of the magnet of the thin band alloy sample of an example, and the example of a comparison, and temperature.

[Drawing 16] When the magnet of the thin band alloy sample of an example and the example of a

comparison is used in the configuration set to $p=10$, respectively, it is drawing showing the temperature change of Ir.

[Drawing 17] Fe88Nb2Nd5 B5 which is within the limits of the presentation of this invention -- the sintering bulk (alloy consolidation object) of a presentation, and Fe86Nb2Pr7 B5 -- it is drawing showing the relation between the permeance coefficient of the thin band alloy of a presentation, and the conventional Nd-Fe-B system magnet, and a temperature coefficient.

[Drawing 18] Fe88Nb2Nd5 B5 which quenched after holding for 180 seconds at the heat treatment temperature of 1023K -- it is the graph which shows the programming rate dependency of the demagnetization curve (the 2nd quadrant) of the thin band alloy sample of a presentation.

[Drawing 19] Fe88Nb2Nd5 B5 which quenched after holding for 180 seconds at the heat treatment temperature of 1023K -- it is drawing showing the programming rate dependency of Ir of the thin band alloy sample of a presentation, Ir/Is, iHc, and BHmax.

[Drawing 20] Fe88Nb2Nd5 B5 which made the programming rate at the time of heat treatment as a part for 3 - 180K/, made the holding time 180 seconds, and quenched after that -- it is drawing showing the heat treatment temperature (retention temperature) dependency of Ir of the thin band alloy sample of a presentation, Ir/Is, and iHc.

[Drawing 21] every which made a part for 3 - 180K/, and retention temperature to 1023K, made the holding time 180 seconds, quenched the programming rate at the time of heat treatment after that, and was obtained -- Fe88Nb2Nd5 B5 -- it is drawing showing the temperature change of magnetization of the thin band alloy sample of a presentation.

[Drawing 22] Fe88Nb2Nd5 B5 which made retention temperature at the time of heat treatment to 1023K, made the holding time 180 seconds, and quenched after that -- it is drawing showing the programming rate dependency of the diameter of average crystal grain of the bcc-Fe phase of the thin band alloy sample of a presentation, and Nd2Fe14 B phase.

[Drawing 23] Fe88Nb2Nd5 B5 obtained by the quenching method -- it is drawing showing the DSC (differential scanning calorimetry) curve in each programming rate of the amorphous alloy thin band sample of a presentation.

[Drawing 24] (a) is drawing showing the crystallization temperature (Tx1) of the bcc-Fe phase of the DSC curve in each programming rate shown in drawing 23, and the crystallization temperature (Tx2) of Nd2Fe14 B phase, and (b) is drawing showing the difference (DTx=Tx2-Tx1) of the crystallization temperature Tx1 of the Tx2 and the bcc-Fe phase of the Nd2Fe14 B phase of a DSC curve in each programming rate shown in drawing 23.

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最終頁に続く

(54)【発明の名称】 硬磁性材料およびその製造方法

(57)【要約】

【課題】 低コストで優れた硬磁気特性を少なくとも備え、さらには優れた温度特性を備えた硬磁性材料の提供。

【解決手段】 Fe, Co, Niのうち1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含み、急冷直後において非晶質相を主相とする合金が10K/分以上の昇温速度で熱処理されてなり、保磁力が1kOe以上である硬磁性材料、及び、Fe, Co, Niのうち1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含み、非晶質相を主相とする合金を液体急冷法により作製した後、該合金を10K/分以上の昇温速度で熱処理する工程を備える硬磁性材料の製造方法。

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【特許請求の範囲】

【請求項1】 Fe, Co, Niのうち1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含み、急冷直後において非晶質相を主相とする合金が10K/分以上の昇温速度で熱処理されてなり、保磁力が1kOe以上である硬磁性材料。

【請求項2】 急冷直後において非晶質相を主相とする合金が10K/分以上の昇温速度で熱処理されてなり、保磁力1kOe以下のソフト磁性相と保磁力1kOe以上のハード磁性相とをそれぞれ10vol(体積)%以上含んでなる保磁力が1kOe以上である硬磁性材料。

【請求項3】 急冷直後において非晶質相を主相とする合金が10K/分以上の昇温速度で熱処理されてなり、キュリー温度が600°C以上の磁性相とキュリー温度が600°C以下の磁性相とをそれぞれ10vol(体積)%以上含んでなる保磁力が1kOe以上である硬磁性材料。

【請求項4】 請求項1～3のいずれかに記載の硬磁性材料において、前記10K/分以上の昇温速度で熱処理後に得られる硬磁性材料は平均結晶粒径100nm以下の微細結晶質相を主相として含むことを特徴とする硬磁性材料。

【請求項5】 請求項1～4のいずれかに記載の硬磁性材料において、急冷直後において非晶質相を主相とする合金が100K/分以上の昇温速度で熱処理されてなることを特徴とする硬磁性材料。

【請求項6】 請求項1～5のいずれかに記載の硬磁性材料は、パーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値が0.10%/K以下のものであることを特徴とする硬磁性材料。

【請求項7】 請求項1～6のいずれかに記載の硬磁性材料は、保磁力が2kOe以上のものであることを特徴とする硬磁性材料。

【請求項8】 請求項1～7のいずれかに記載の硬磁性材料は、飽和磁化(I_s)に対する残留磁化(I_r)の割合(I_r/I_s)が、0.6以上のものであることを特徴とする硬磁性材料。

【請求項9】 請求項1～8のいずれかに記載の硬磁性材料は、下記組成式を有し、かつ、残留磁化(I_r)が100emu/g以上のものであることを特徴とする硬磁性材料。

T_xM_yR_zB_w

ただし、TはFe, Co, Niのうち1種以上の元素を表わし、MはZr, Nb, Ta, Hfのうち1種以上の元素を表わし、Rは希土類元素のうち1種以上の元素を表わすとともに、組成比を示すx, y, z, wは原子%で、5.0≤x, 0≤y≤1.5, 3≤z≤2.0, 3≤w≤2.0である。

【請求項10】 前記組成式中の組成比を示すx, y, z, wは原子%で、8.6≤x≤9.2, 0.5≤y≤3,

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3≤z≤7, 3≤w≤7であることを特徴とする請求項9記載の硬磁性材料。

【請求項11】 請求項1～8のいずれかに記載の硬磁性材料は、下記組成式を有することを特徴とする硬磁性材料。

T_xM_yR_zB_wE_v

ただし、TはFe, Co, Niのうち1種以上の元素を表わし、MはZr, Nb, Ta, Hfのうち1種以上の元素を表わし、Rは希土類元素のうち1種以上の元素を表わし、EはCr, Al, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, Geのうち1種以上の元素を表わすとともに、組成比を示すx, y, z, w, vは原子%で、5.0≤x, 0≤y≤1.0, 3≤z≤1.5, 3≤w≤2.0, 0≤v≤1.0である。

【請求項12】 前記組成式中の組成比を示すx, y, z, w, vは原子%で、8.0≤x≤9.2, 1≤y≤5, 4≤z≤1.0, 3≤w≤7, 0≤v≤5であることを特徴とする請求項11記載の硬磁性材料。

【請求項13】 請求項1～12のいずれかに記載の硬磁性材料において、SiがT元素置換で0.5～5原子%添加されてなることを特徴とする硬磁性材料。

【請求項14】 Fe, Co, Niのうち1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含み、非晶質相を主相とする合金を液体急冷法により作製した後、該合金を10K/分以上の昇温速度で熱処理する工程を備えることを特徴とする硬磁性材料の製造方法。

【請求項15】 請求項14に記載の硬磁性材料の製造方法において、液体急冷法により作製した非晶質相を主相とする合金を10K/分以上の昇温速度で熱処理することにより該合金中に平均結晶粒径100nm以下の微細結晶質相を主相として析出させることを特徴とする硬磁性材料の製造方法。

【請求項16】 請求項14～15のいずれかに記載の硬磁性材料の製造方法において、液体急冷法により得られた非晶質相を主相とする合金を100K/分以上の昇温速度で熱処理することを特徴とする硬磁性材料の製造方法。

【請求項17】 請求項14～16のいずれかに記載の硬磁性材料の製造方法において、下記組成式を有する非晶質相を主相とする合金を熱処理することを特徴とする硬磁性材料の製造方法。

T_xM_yR_zB_w

ただし、TはFe, Co, Niのうち1種以上の元素を表わし、MはZr, Nb, Ta, Hfのうち1種以上の元素を表わし、Rは希土類元素のうち1種以上の元素を表わすとともに、組成比を示すx, y, z, wは原子%で、5.0≤x, 0≤y≤1.5, 3≤z≤2.0, 3≤w≤2.0である。

【請求項18】 前記組成式中の組成比を示すx, y,

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z, w は原子%で、 $8.6 \leq x \leq 9.2$ 、 $0.5 \leq y \leq 3$ 、 $3 \leq z \leq 7$ 、 $3 \leq w \leq 7$ であることを特徴とする請求項17記載の硬磁性材料の製造方法。

【請求項19】 請求項14～16のいずれかに記載の硬磁性材料の製造方法において、下記組成式を有する非晶質相を主相とする合金を熱処理することを特徴とする硬磁性材料の製造方法。

$T_x M_y R_z B_w E_v$

ただし、TはFe, Co, Niのうち1種以上の元素を表わし、MはZr, Nb, Ta, Hfのうち1種以上の元素を表わし、Rは希土類元素のうち1種以上の元素を表わし、EはCr, Al, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, Geのうち1種以上の元素を表わすとともに、組成比を示すx, y, z, w, vは原子%で、 $5.0 \leq x \leq 9.2$ 、 $0 \leq y \leq 1.0$ 、 $3 \leq z \leq 1.5$ 、 $3 \leq w \leq 2.0$ 、 $0 \leq v \leq 1.0$ である。

【請求項20】 前記組成式中の組成比を示すx, y, z, w, vは原子%で、 $8.0 \leq x \leq 9.2$ 、 $1 \leq y \leq 5$ 、 $4 \leq z \leq 1.0$ 、 $3 \leq w \leq 7$ 、 $0 \leq v \leq 5$ であることを特徴とする請求項19記載の硬磁性材料の製造方法。

【請求項21】 請求項14～20のいずれかに記載の硬磁性材料の製造方法において、前記非晶質相を主相とする合金にSiをT元素置換で0.5～5原子%添加した合金を熱処理することを特徴とする硬磁性材料の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、磁気式エンコーダ、ポテンショメータ等のセンサ、モータ、アクチュエータ、スピーカなどに使用できる磁気性能に優れた硬磁性材料およびその製造方法に関する。

【0002】

【従来の技術】 一般に、フェライト磁石やアルニコ(A-Ni-Co-Fe系)よりも優れた性能を有する磁石材料としては、Sm-Co系磁石、Nd-Fe-B系磁石などが知られており、またさらに高い性能を目指してSm-Fe-N系磁石などの新しい合金磁石の研究も数多くなされている。

【0003】

【発明が解決しようとする課題】 しかしながら、これらの磁石材料においては、10at%以上のNd、または8at%以上のSmが必要であり、高価な希土類元素の使用量が多いことからフェライト磁石やアルニコ磁石よりも製造コストが高くなってしまうという欠点があった。さらに、Nd-Fe-B系磁石は、温度による磁気特性の変化が大きいためセンサとしては使用できないという問題があった。また、Sm-Co系磁石は、磁化の温度係数の絶対値が小さい磁石であるが、Nd-Fe-B系磁石よりも高価な磁石であるため、使用できる範囲が限られていた。一方、フェライト磁石は、上述のよう

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に希土類磁石に比べてコストは低いものの、磁化の温度係数の絶対値が大きいためセンサとしては使用できないという問題があった。また、アルニコ(A1-Ni-Co-Fe系)磁石は、磁化の温度係数の絶対値は小さく、しかもコストは低いものの、保磁力が小さいため実用化が困難であった。このため、低成本でフェライト磁石以上の硬磁気特性を少なくとも備え、さらには温度特性が優れた磁石材料の出現が望まれていた。

【0004】 そこで、本願発明者らは、低成本で高い硬磁気特性を示す硬磁性材料を得るために特願平8-68822号、特願平8-242356などにおいて特許出願を行っている。これらの特許出願に記載された技術によれば、Feを主成分とし、Zr, Nb, Ta, Hfのうち1種または2種以上からなる元素Mと、希土類元素のうちの1種または2種以上からなる元素Rと、Bとを含む非晶質合金を液体急冷法を用いて作製した後、該非晶質合金を600～900°Cで熱処理して、bccのFeと、Fe-Bの化合物および/またはR₂Fe₁₄B₁を主体とする平均結晶粒径100nm以下の微細結晶相を析出させることで、残留磁化(I_r)が0.8～1.3T、保磁力(I_{Hc})が170～400kA/m、最大磁気エネルギー積((BH)_{max})が60～110kJ/m³の比較的高い硬磁気特性を示す硬磁性材料が製造できる。以上のような合金の研究の基で本発明者らは、低成本で、硬磁気特性が優れた硬磁性材料を製造するために、特に、急冷後の非晶質相を主相とする合金を熱処理する際の昇温速度に着目し、種々の検討及び実験を重ねた結果、非晶質相を主相とする合金の昇温速度と、熱処理により析出する微細結晶相のナノ結晶構造(特にbcc-Fe相の結晶粒径)および硬磁気特性とは相関があることを発見し、本発明に到達したのである。さらに、本発明者らは、温度特性が優れた硬磁性材料を製造するために、種々の検討及び実験を重ねた結果、パーキンス係数(p)と磁化の温度係数とは相関があることを発見し、本発明に到達したのである。

【0005】 本発明は上記事情に鑑みてなされたもので、低成本で優れた硬磁気特性を少なくとも備え、さらには優れた温度特性を備えた硬磁性材料を提供できるようにすることを目的とする。

【0006】

【課題を解決するための手段】 本発明は、Fe, Co, Niのうち1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含み、急冷直後において非晶質相を主相とする合金が10K/分以上の昇温速度で熱処理されてなり、保磁力が1kOe以上である硬磁性材料を上記課題の解決手段とした。また、本発明は、急冷直後において非晶質相を主相とする合金が10K/分以上の昇温速度で熱処理されてなり、保磁力1kOe以下のソフト磁性相と保磁力1kOe以上のハード磁性相とをそれぞれ10vol(体積)%以上含んでな

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る保磁力が1 kOe以上である硬磁性材料を上記課題の解決手段とした。また、本発明は、急冷直後において非晶質相を主相とする合金が10 K/分以上の昇温速度で熱処理されてなり、キュリー温度が600°C以上の磁性相とキュリー温度が600°C以下の磁性相とをそれぞれ10 vol(体積)%以上含んでなる保磁力が1 kOe以上である硬磁性材料を上記課題の解決手段とした。

【0007】上記急冷直後において非晶質相を主相とする合金を10 K/分以上の昇温速度で熱処理した後に得られる硬磁性材料は、平均結晶粒径100 nm以下の微細結晶質相を主相として含むことが好ましい。上記急冷直後において非晶質相を主相とする合金は、100 K/分以上の昇温速度で熱処理されることが好ましい。上記の構成の硬磁性材料は、パーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値が0.10%/K以下のものであることが好ましい。上記の構成の硬磁性材料は、保磁力が2 kOe以上のものであることが好ましい。上記の構成の硬磁性材料は、飽和磁化(I_s)に対する残留磁化(I_r)の割合(I_r/I_s)が、0.6以上のものであることが好ましい。

【0008】上記の構成の硬磁性材料は、下記組成式を有し、かつ、残留磁化(I_r)が100 emu/g以上のものであることが好ましい。

T_xM_yR_zB_w

ただし、TはFe, Co, Niのうち1種以上の元素を表わし、MはZr, Nb, Ta, Hfのうち1種以上の元素を表わし、Rは希土類元素のうち1種以上の元素を表わすとともに、組成比を示すx, y, z, wは原子%で、50≤x, 0≤y≤15, 3≤z≤20, 3≤w≤20である。さらに、上記組成式中の組成比を示すx, y, z, wは原子%で、86≤x≤92, 0.5≤y≤3, 3≤z≤7, 3≤w≤7であることが好ましい。

【0009】また、上記の構成の硬磁性材料は、下記組成式を有するものであってもよい。

T_xM_yR_zB_wE_v

ただし、TはFe, Co, Niのうち1種以上の元素を表わし、MはZr, Nb, Ta, Hfのうち1種以上の元素を表わし、Rは希土類元素のうち1種以上の元素を表わし、EはCr, Al, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, Geのうち1種以上の元素を表わすとともに、組成比を示すx, y, z, w, vは原子%で、50≤x, 0≤y≤10, 3≤z≤15, 3≤w≤20, 0≤v≤10である。さらに、上記組成式中の組成比を示すx, y, z, w, vは原子%で、80≤x≤92, 1≤y≤5, 4≤z≤10, 3≤w≤7, 0≤v≤5であることが好ましい。また、本発明の硬磁性材料には、SiがT元素置換で0.5~5原子%添加されたものであってもよい。

【0010】上記課題を解決するために本発明の硬磁性材料の製造方法は、Fe, Co, Niのうち1種以上の

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元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含み、非晶質相を主相とする合金を液体急冷法により作製した後、該合金を10 K/分以上の昇温速度で熱処理する工程を備えることによって、上記合金中に析出する微細結晶質相のbcc-Fe相の平均結晶粒径が微細化し、これによってソフト磁性相(bcc(体心立方構造)-Fe)とハード磁性相(R₂Fe₁₄B)の交換結合特性が向上し、残留磁化(I_r)、角型比(I_r/I_s)、保磁力(iHc)、最大磁気エネルギー積((BH)_{max})が増加し、硬磁性特性が優れた硬磁性材料が得られる。

【0011】また、上記の構成の硬磁性材料の製造方法においては、液体急冷法により作製した非晶質合金を主相とする合金を10 K/分以上の昇温速度で熱処理することにより、合金中に平均結晶粒径100 nm以下の微細結晶質相を主相として析出させることが好ましい。さらに、上記の構成の硬磁性材料の製造方法においては、液体急冷法により得られた非晶質相を主相とする合金を熱処理する際の昇温速度を100 K/分以上とすることが好ましい。

【0012】上記昇温速度で熱処理される合金としては、下記組成式を有する非晶質相を主相とする合金を用いることが好ましい。

T_xM_yR_zB_w

ただし、TはFe, Co, Niのうち1種以上の元素を表わし、MはZr, Nb, Ta, Hfのうち1種以上の元素を表わし、Rは希土類元素のうち1種以上の元素を表わすとともに、組成比を示すx, y, z, wは原子%で、50≤x, 0≤y≤15, 3≤z≤20, 3≤w≤20である。ここで用いられる合金の組成式中の組成比を示すx, y, z, wは原子%で、86≤x≤92, 0.5≤y≤3, 3≤z≤7, 3≤w≤7であることが好ましい。

【0013】また、上記昇温速度で熱処理される合金としては、下記組成式を有する非晶質相を主相とする合金を用いてもよい。

T_xM_yR_zB_wE_v

ただし、TはFe, Co, Niのうち1種以上の元素を表わし、MはZr, Nb, Ta, Hfのうち1種以上の元素を表わし、Rは希土類元素のうち1種以上の元素を表わし、EはCr, Al, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, Geのうち1種以上の元素を表わすとともに、組成比を示すx, y, z, w, vは原子%で、50≤x, 0≤y≤10, 3≤z≤15, 3≤w≤20, 0≤v≤10である。ここで用いられる合金の組成式中の組成比を示すx, y, z, w, vは原子%で、80≤x≤92, 1≤y≤5, 4≤z≤10, 3≤w≤7, 0≤v≤5であることが好ましい。また、上記昇温速度で熱処理される合金としては、上記組成の非晶質相を主相とする合金にSiをT元素置換で

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0.5～5原子%添加した合金を用いてよい。

【0014】

【発明の実施の形態】以下、本発明の実施の形態について詳しく説明する。本発明に係わる硬磁性材料は、Fe, Co, Niのうち1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含み、急冷直後において非晶質相を主相とする合金が10K/分以上の昇温速度で熱処理されてなり、保磁力が1kOe以上のものである。上記の非晶質相を主相とする合金を10K/分以上の昇温速度で熱処理後に得られる硬磁性材料は、平均結晶粒径100nm以下の微細結晶質相を主相として含んでいる。この微細結晶質相は、平均結晶粒径100nm以下のbcc-Fe相と、平均結晶粒径100nm以下のR₂Fe₁₄B相が析出している。また、この硬磁性材料は、上記のbcc-Fe相とR₂Fe₁₄B相とFe₃B相を主体とする微細結晶質相と、残留した非晶質相とのナノ複相組織を形成している。

【0015】さらに、本発明の硬磁性材料は、保磁力1kOe以下のソフト磁性相と保磁力1kOe以上のハード磁性相とをそれぞれ10v/o(体積)%以上含んでなることが、ソフト磁性相とハード磁性相の中間の特性を備えることができる点で好ましい。保磁力1kOe以下のソフト磁性相が10v/o(体積)%未満であると、合金の保磁力は大きくなるがハード磁性相を構成するのに必要な希土類元素の濃度が高くなるため好ましくない。また、保磁力1kOe以上のハード磁性相が10v/o(体積)%未満であると、合金の保磁力が小さくなるため好ましくない。

【0016】また、本発明の硬磁性材料が、キュリー温度が600℃以上の磁性相とキュリー温度が600℃以下の磁性相とをそれぞれ10v/o(体積)%以上含んでなることがソフト磁性相とハード磁性相の中間の特性を備えることができる点で好ましい。それは、bcc-Fe相のキュリー温度は770℃付近であり、R₂Fe₁₄B相のキュリー温度が315℃付近であることから、本発明の硬磁性材料が磁化に関与する相であるソフト磁性相とハード磁性相との2相を有するためには、キュリー温度が600℃以上の磁性相とキュリー温度が600℃以下の磁性相とを含む必要がある。各磁性相の磁化の絶対値の温度変化は、その相のキュリー温度が高い方が小さく、このようにキュリー温度が高い相(ソフト磁性相)を10v/o(体積)%以上含有していると高いペーミアンスでの磁化の温度変化が小さくなるという特徴を持つことができる。キュリー温度が600℃以上の磁性相が10v/o(体積)%未満であると、比較的高いペーミアンスで使用したときの磁化の温度変化が大きくなるため好ましくない。また、キュリー温度が600℃以下の磁性相が10v/o(体積)%未満であると、ハード磁性相が少なくなるため、保磁力が低くなり好ましくない。

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【0017】本発明に係わる硬磁性材料においては、上記急冷直後において非晶質相を主相とする合金は100K/分以上の昇温速度で熱処理されることがbcc-Feの平均結晶粒径を細かくし、硬磁性特性を向上させる点で好ましい。

【0018】ところで、磁石材料の特性は、ヒステリシス曲線の第2象限の部分、すなわち減磁曲線によって表される。着磁後の磁石材料は、自身の残留磁化がつくる逆向きの磁界、反磁界の下にあるので、その動作点(材料の磁束密度(B)と減磁界(H))は、減磁曲線上の一点pによって与えられる。ここでB/μ₀Hの値(無次元の数)をペーミアンス係数(p)、pと原点O間の線(OP)をペーミアンス線とよぶ。このペーミアンス係数(p)あるいはペーミアンス線は、磁石の形状に依存し、磁化方向の長さが短くなると、小さくなり、長くなると大きくなるものである。ペーミアンス係数と反磁界係数(N)との間には、下記式(I)

$$p = (1 - N) / N \quad \dots \quad (I)$$

で示される関係がある。従って、減磁曲線と磁石材料の形状が与えられると、その動作点(B, H)は決定される。その磁石材料が外部につくる静磁界のエネルギーは、下記式(II)

$$U = BHV / 2 \quad \dots \quad (II)$$

(式中、Vは磁性材料の体積)で与えられる。磁石材料の形状が変化すると、反磁界、すなわちペーミアンス線が変化するので、動作点pが変化し上記Uの値が変化する。途中ある動作点p_mでUの値が最大となり、そのときの(BH)の積が最大磁気エネルギー積((BH)_{max})である。

【0019】本発明に係わる硬磁性材料をセンサ等に使用する場合、10以上のペーミアンス係数で使用したときの磁化の温度係数の絶対値が0.10%/K以下のものであることが好ましい。硬磁性材料をセンサ等に使用する場合は、温度特性が優れるものすなわち磁化の温度係数の絶対値が小さいもの(磁化の温度変化が小さいもの)を用いることが好ましく、本発明の硬磁性材料はペーミアンス係数が10以上となるような形状で使用したときの磁化の温度係数の絶対値が0.10%/K以下と小さくなるので、センサ等に好適に使用することができ、ペーミアンス係数が10未満の形状で使用すると磁化の温度係数の絶対値が大きくなってしまう。また、本発明の硬磁性材料は、ペーミアンス係数が20以上となるような形状で使用するのが、磁化の温度係数の絶対値が0.08%/K以下となる点でより好ましい。

【0020】このような温度特性が優れた本発明の硬磁性材料は、後述するようにSi元素T元素置換で0.5～5原子%(at%)添加あるいはT元素中にCoが0.5～20%含まれるようにすることにより、従来のNd-Fe-B系の磁石(p=10のときの温度係数が-0.11～-0.13%/K)に対して、p=10以

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上のときの磁化の温度係数の絶対値が0.10%／K以下と小さいものを実現することができる。さらに、本発明の硬磁性材料は、フェライト磁石やアルニコ磁石より保磁力が大きく、また、従来から温度特性が良好なものとして使用されているSm-Co系磁石よりも安価である。

【0021】さらに、本発明に係わる硬磁性材料は、保磁力が2kOe以上のものであることが好ましい。また、本発明に係わる硬磁性材料は、飽和磁化(I_s)に対する残留磁化(I_r)の割合である角型比(I_r/I_s)が、0.6以上のものであることが好ましい。ここで、本発明における飽和磁化(I_s)は、十分高い外部磁場下で、磁化曲線を測定したときに試料の磁化がほぼ飽和するときの値である。上述のような硬磁性材料中の結晶質相の平均結晶粒径、および各相中における各原子の濃度の制御は、非晶質合金を熱処理して硬磁性材料を得る際の熱処理条件を制御することによって実現できる。熱処理条件は、昇温速度、熱処理温度(アニール温度)及びその保持時間などである。

【0022】本発明に係わる硬磁性材料は、以下の組成式で表すことができる。

T_xMyR_zB_w

上記組成式中のTはFe, Co, Niのうち1種以上の元素を表わす。これらの元素は、本発明に係る硬磁性材料の主成分であり、磁性を担う元素である。Tの組成比xを増加させると、それに伴って飽和磁化(I_s)が増加する。100emu/g以上の高い残留磁化(I_r)を実現するためには、飽和磁化(I_s)が少なくとも130emu/gは必要であり、これを満たすにはTの濃度は50at%以上とするのが好ましく、120emu/g以上のさらに高い残留磁化(I_r)を得るためにTの濃度は80at%、好ましくは86at%以上の範囲であるのが望ましい。また、優れた硬磁気特性を得るためにTの濃度は92at%以下とするのが好ましい。本発明の硬磁性材料においては、元素Tの少なくとも一部としてFeが含まれていることが必要である。なお、後述する様に、本発明の実施例における試料の密度は、ほぼ7.6g/cm³であり、例えば、100emu/gであれば、100(emu/g) × 4π × 7.6(g/cm³) × 0.0001 = 0.95(T)と換算することができる。従って、emu/gで表記した場合、その材料固有の磁化とみることができる。

【0023】上記組成式中のMはZr, Nb, Ta, Hfのうち1種以上の元素を表わし、これらの元素は非晶質形成能が高いものである。本発明に係る硬磁性材料において、Mを添加することにより、希土類元素(R)が低濃度の場合も非晶質相を形成することができる。希土類元素(R)置換でMの組成比yを増加させると、それに伴って残留磁化(I_r)は増加するが、保磁力(iHc)が低下し、硬磁気特性から軟磁気特性へと変化す

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る。また、磁性を担う元素(T)置換で非晶質形成元素(M)を増加させると、飽和磁化(I_s)、残留磁化(I_r)の減少が生じる。従って、良好な硬磁気特性を得るために、Mの濃度(y)は0at%以上15at%以下、好ましくは0.5at%以上3at%以下の範囲とするのが好ましい。

【0024】上記組成式中のRは希土類金属(Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb、およびLu)のうちの1種以上の元素を表わす。RとFeとBとを含む非晶質合金を873～1173Kの範囲の適切な温度で加熱したときに析出する金属間化合物R₂Fe₁₄B₁は、本発明の材料に優れた硬磁気特性を付与するものである。Rの組成比zを増加させると、それに伴って飽和磁化(I_r)が減少する。100emu/g以上の高い残留磁化(I_r)を得るために、飽和磁化(I_s)が少なくとも130emu/gは必要であり、これを満たすにはRの濃度(z)は20at%以下、好ましくは7at%以下の範囲とすることが望ましい。またRは非晶質を形成し易い元素であり、Rの組成比が小さ過ぎると良好な非晶質相または微細結晶質相を得られないため、Rの濃度としては3at%以上とするのが望ましい。さらにRの一部または全部をNdおよび/またはPrで構成すると、さらに高い硬磁気特性が得られる。

【0025】上記組成式中のBは、非晶質を形成し易い元素である。またFeとBとを含む非晶質相を873～1173Kの範囲の適切な温度で熱処理したときに析出する化合物R₂Fe₁₄Bは、本発明の材料に硬磁気特性を付与するものである。良好な非晶質相または微細結晶質相を得るために、Bの濃度を3at%以上の範囲とするのが望ましいが、Bの組成比(w)の増加に伴って飽和磁化(I_s)、残留磁化(I_r)、および保磁力(iHc)が減少するので、良好な硬磁気特性を得るために、Bの濃度は20at%以下、好ましくは7at%以下の範囲とすることが望ましい。

【0026】また、本発明の硬磁性材料には、Cr, Al, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, Geのうち1種以上の元素Eが添加されていてもよく、その場合の硬磁性材料は、下記の組成式で表すことができる。TxMyRzBwEvこの場合の磁性を担う元素Tの濃度xは、100emu/g以上の高い残留磁化を得るために飽和磁化(I_s)を増加させる点で50at%以上とするのが好ましく、120emu/g以上のさらに高い残留磁化(I_r)と優れた硬磁気特性を両立するためには80at%以上92at%以下が好ましく、より好ましくは86at%以上92at%以下である。上記組成式中のMの濃度は、良好な硬磁気特性を得るために、好ましくは0at%以上10at%以下、より好ましくは1at%以上5at%以下であり、120emu/g以上の高い残留磁化(I_r)を実

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現するためには、0.5 at%以上3 at%以下するのが好ましい。

【0027】上記組成式中のRの濃度は、本発明の材料に優れた硬磁気特性を付与するためと、良好な非晶質相または微細結晶質相を得るために、好ましくは3 at%以上15 at%以下、より好ましくは4 at%以上10 at%以下であり、120 emu/g以上の高い残留磁化(I_r)を実現するためには、3 at%以上7%以下とするのが好ましい。上記組成式中のBの濃度は、良好な非晶質相または微細結晶質相を得るために、3 at%以上とすることが望ましい。また、良好な硬磁気特性を得るために、Bの濃度は、好ましくは20 at%以下、より好ましくは7 at%以下とされる。元素Eが添加されることによって硬磁性材料の耐食性が向上する。ただし、元素Eの濃度が高過ぎると硬磁気特性が劣化するので、Eの濃度は、好ましくは10 at%以下、より好ましくは5 at%以下とされる。また、優れた耐食性を得るために、元素Eは少なくとも1 at%以上添加するのが好ましい。また、120 emu/g以上の高い残留磁化(I_r)を達成するためには、Eを添加しない方が好ましい。

【0028】また、本発明の硬磁性材料において、T元素中にFe以外にCoが含まれるようすれば、特に、バーミアンス係数(p)が10以上となるような形状で使用したときの磁化の温度係数の絶対値を小さくすることができる。Co元素の含有量は、合金の原料コストおよび磁化の大きさに変化をもたらすので、T元素全体に占めるCo元素の割合は、好ましくは50%以下、より好ましくは0.5%以上20%以下、さらに好ましくは5%以上20%以下の範囲とされ、合金の組成や熱処理条件等に応じて適宜設定するのが好ましい。

【0029】また、本発明の硬磁性材料において、Si元素をT元素置換で添加すれば、磁気特性、特に保磁力(iHc)、および最大磁気エネルギー積((BH)_{max})をさらに向上させることができ、また、バーミアンス係数(p)が10以上となるような形状で使用したときの磁化の温度係数の絶対値を低くすることができる。Si元素の添加量は、多過ぎるとT元素の組成比が低くなるために硬磁性材料の磁気特性がかえって低下するので、好ましくは0.5 at%以上5 at%以下、より好ましくは0.5 at%以上3 at%以下の範囲とされ、合金の組成や熱処理条件等に応じて適宜設定するのが好ましい。このようにして保磁力および温度特性が改善された硬磁性材料は、特に、小型モータ用磁石、センサとして好適に用いられる。

【0030】つぎに、本発明に係わる硬磁性材料は、以下のようにして製造することができる。上述のような非晶質合金を得る方法は、回転ドラムに溶湯を吹き付けて急冷して薄帯状に形成する方法、溶湯を冷却用気体中に噴出して液滴状態で急冷して粉末状に形成する方法など

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の液体急冷法、あるいはスパッタリングやCVD法による方法等を用いることができる。また、上記非晶質合金に対する熱処理は、任意の加熱手段を用いて行なうことができ、例えば本発明の硬磁性材料からなる圧密体を得る場合には、まず非晶質合金を粉末状にし、その合金粉末をホットプレスにより加圧成形すると同時に適切な昇温速度および熱処理温度(アニール温度)で熱処理する方法を好ましく用いることができる。

【0031】熱処理時の昇温速度は、10 K/分以上、10好ましくは100 K/分以上の範囲で、非晶質合金の組成により好ましく設定される。熱処理時の昇温速度が10 K/分未満であると、熱処理により合金中に析出する結晶粒が粗大化するため、ソフト磁性相(bcc(体心立方構造)-Fe)とハード磁性相(R₂Fe₁₄B)の交換結合特性が低下し、硬磁気特性が劣化するため好ましくない。また、熱処理時の昇温速度を100 K/分以上の範囲とすることにより、より均一な微細組織の形成が可能となる。なお、昇温速度の上限としては、装置上の制約から、200 K/分程度とされる。

【0032】熱処理時の熱処理温度(アニール温度)は、好ましくは873 K~1173 K、より好ましくは973 K~1023 Kの範囲、保持時間(熱処理時間)は好ましくは1~20分、より好ましくは3~10分の範囲で、非晶質合金の組成により好ましく設定される。熱処理温度が873 K未満であると、硬磁気特性を担うR₂Fe₁₄B相の析出量が少ないため十分な硬磁気特性が得られず、好ましくない。一方、熱処理温度が1173 Kを越えると、他の析出物が析出するか、または結晶粒の粗大化がおこり、硬磁気特性が低下してしまうため好ましくない。

【0033】上記非晶質合金としては、組成がTxMyRzBwであり、組成比を示すx, y, z, wは原子%で50≤x、0≤y≤15、3≤z≤20、3≤w≤20なる関係を満足するものを用いること、より好ましくは原子%で86≤x≤92、0.5≤y≤3、3≤z≤7、3≤w≤7なる関係を満足するものを用いることにより、希土類元素の濃度が低くても急冷状態で良好な非晶質相が得られ、この後、10 K/分以上の昇温速度で熱処理されることより硬磁気特性を付与する化合物が析出されるので、低コストで優れた硬磁気特性を有する硬磁性材料を得ることができる。また、上記非晶質合金としては、組成がTxMyRzBwEvであり、組成比を示すx, y, z, w, vは原子%で、50≤x、0≤y≤10、3≤z≤15、3≤w≤20、0≤v≤10なる関係を満足するものを用いるのが、熱処理後に得られる硬磁性材料に耐食性も備えることができる点で好ましい。また、ここでの組成式中の組成比を示すx, y, z, w, vは、原子%で、80≤x≤92、1≤y≤5、4≤z≤10、3≤w≤7、0≤v≤5なる関係を満足することにより、より硬磁気特性が優れた硬磁気材料を得

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することができる。

【0034】また、上記非晶質合金としては、Si元素をT元素置換で0.5~5原子%添加したもの、あるいはT元素中にFe以外にCoを含ませたものを用いるのが、熱処理後に得られる硬磁性材料をパーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値が0.10%/K以下のものを得ることができるので好ましい。

【0035】このようにして得られた硬磁性材料にあっては、特に、上記の急冷直後において非晶質相を主相とする合金が10K/分以上の昇温速度で熱処理されることにより、 $R_2Fe_{14}B$ 相の結晶化温度とbcc-Fe相の結晶化温度の差が小さく、bcc-Fe相と $R_2Fe_{14}B$ 相を同時に結晶化できる傾向が強いためにどちらかの結晶相が粗大化するのを防止することができ、上記合金中に析出する微細結晶質相のbcc-Fe相と $R_2Fe_{14}B$ 相の平均結晶粒径を微細化することができる。さらに、 $R_2Fe_{14}B$ 相はbcc-Fe相より平均結晶粒径が小さいうえ、bcc-Fe相より昇温速度に大きく依存するので、熱処理時の昇温速度を10K/分以上とすることにより、bcc-Feの粒子と $R_2Fe_{14}B$ の粒子が隣り合う確率が多くなり、ソフト磁性相(bcc(体心立方構造)-Fe)とハード磁性相($R_2Fe_{14}B$)の交換結合が行われ易くなるために交換結合特性が向上し、残留磁化(Ir)、角型比(Ir/Is)、保磁力(iHc)、最大磁気エネルギー積((BH)max)が増加し、優れた硬磁気特性が得られる。具体的には、1T以上の残留磁化(Ir)を有する硬磁性材料、1kOe以上の保磁力(iHc)を有する硬磁性材料、角型比(Ir/Is)が0.6以上の硬磁性材料、最大磁気エネルギー積((BH)max)が60kJ/m³を越える優れた硬磁性材料を実現することができる。

【0036】さらに、本発明に係わる硬磁性材料は、希土類元素Rの含有量を少なくしても優れた硬磁気特性が得られるので、比較的低い製造コストで製造することができる。また、本発明に係わる硬磁性材料にあっては、Si元素をT元素置換で0.5~5原子%添加、あるいはT元素中にFe以外にCoが0.5~20%含まれる

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ようにすることにより、パーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値が0.10%/K以下のものを実現することができ、温度特性を向上させることができる。従って、本発明に係わる硬磁性材料は、磁気式ロータリーエンコーダやポテンショメータなどのセンサ、アクチュエータ、スピーカ、モータなどに好適に用いることができる。

【0037】

【実施例】

【実験例1】以下のようにして、各種組成の急冷薄帯合金を熱処理するに際して昇温速度を変更して硬磁性材料を作製した。まず、アーク溶解法によりインゴットを作製し、Ar雰囲気中において回転しているCuロール上に、溶解した金属をスリット径約0.3mmの細幅ノズルから吹出すことにより、約20μmの厚さの急冷薄帯合金を作製した。得られた急冷薄帯合金の密度は、7.6g/cm³であった。次いで、得られた急冷薄帯合金を1×10⁻²Pa以下の赤外線イメージ炉中において、昇温速度3~216K/分で加熱し、973K又は1023Kで約180秒間保持する条件で熱処理して得られる薄帯合金試料の磁気特性およびナノ結晶構造に及ぼす影響について調べた。ここで得られた薄帯合金試料の組成は、いずれも本発明の範囲内にある $Fe_{88}Nb_2Pr_5B_5$ なる組成の薄帯合金、 $Fe_{88}Nb_2Nd_5B_5$ なる組成の薄帯合金であった。結果を下記表1~表4に示す。なお、表1~表4中、Ir/Isは飽和磁化に対する残留磁化の割合である。

【0038】得られた薄帯合金試料の磁気特性はVSM(振動試料型磁力計)を用い、15kOeの印加磁場中で室温にて測定した。試料によっては、15kOeの印加磁場では磁化が飽和していない場合もあるが、本説明の中ではほぼ飽和しているものとして飽和磁化として取り扱った。また、ナノ結晶構造の解析は、bcc-Fe相の格子定数をX線回折ピークより計算し、bcc-Fe相の平均結晶粒径をX線回折ピークの半価幅よりシェラーの式を用いて計算することにより行った。

【0039】

【表1】

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Fe₈₈Nb₂Pr₅B₅(973K)

サンプルNo.	磁気特性 昇温 速度 (K/分)	残留 磁化 (T)	Ir/Is	保磁力 kOe	最大磁気 工率 ^{1/2} 一積 (kJ/m ³)	格子定数 (nm)	平均結晶 粒径 (nm)
1 (実施例)	180	1.46	0.83	2.17	91	0.2871	35
2 (実施例)	102	1.45	0.82	1.79	74	0.2872	36
3 (実施例)	36	1.38	0.78	2.33	82	0.28695	43
4 (実施例)	18	1.39	0.78	1.90	67	0.28719	46
5 (比較例)	6	1.15	0.66	1.99	51	0.28731	48
6 (比較例)	3	1.12	0.64	1.88	48	—	—

【0040】

* * 【表2】

Fe₈₈Nb₂Pr₅B₅(1023K)

サンプルNo.	磁気特性 昇温 速度 (K/分)	残留 磁化 (T)	Ir/Is	保磁力 kOe	最大磁気 工率 ^{1/2} 一積 (kJ/m ³)	格子定数 (nm)	平均結晶 粒径 (nm)
7 (実施例)	180	1.37	0.76	2.44	81	0.28727	35.2
8 (実施例)	102	1.28	0.74	1.91	52	0.28727	34.7
9 (実施例)	36	1.33	0.74	2.43	75	0.28707	37.2
10 (実施例)	18	1.26	0.70	1.64	37	0.28714	45.6
11 (比較例)	6	1.15	0.64	1.32	23	0.28711	46
12 (比較例)	3	1.11	0.62	1.26	21	—	—

【0041】

【表3】

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Fe₈₈Nb₂Nd₅B₅(973K)

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サンプルNo.	磁気特性	昇温速度 (K/分)	残留 磁化 (T)	Ir/Is	保磁力 kOe	最大磁気 エネルギー積 (kJ/m ³)	格子定数 (nm)	平均結晶 粒径 (nm)
13 (実施例)		180	1.38	0.84	1.86	83	0.2871	27
14 (実施例)		102	1.34	0.81	1.90	81	0.28682	26
15 (実施例)		36	1.32	0.79	1.85	75	0.28705	33
16 (実施例)		18	1.28	0.77	1.54	43	0.28719	42
17 (比較例)		6	1.11	0.66	2.00	57	0.2875	37
18 (比較例)		3	1.05	0.69	1.82	23	—	—

【0042】

* * 【表4】

Fe₈₈Nb₂Nd₅B₅(1023K)

サンプルNo.	磁気特性	昇温速度 (K/分)	残留 磁化 (T)	Ir/Is	保磁力 kOe	最大磁気 エネルギー積 (kJ/m ³)	格子定数 (nm)	平均結晶 粒径 (nm)
19 (実施例)		180	1.5	0.81	2.46	119	0.2873	28.9
20 (実施例)		102	1.48	0.80	2.37	102	0.28714	32.4
21 (実施例)		36	1.32	0.71	2.05	54	0.28714	37.4
22 (実施例)		18	1.36	0.73	2.21	83	0.28715	29.5
23 (比較例)		6	1.17	0.62	2.16	46	0.2873	35.1
24 (比較例)		3	1.09	0.58	2.01	32	—	—

【0043】図1～図2は973K～1023Kで熱処理後におけるFe₈₈Nb₂Pr₅B₅なる組成の薄帯合金試料及びFe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料のbcc-Fe相の格子定数及び平均結晶粒径の昇温速度依存性を示す図である。図3～図4は、973K～1023Kの熱処理温度で5分間保持した後、昇温速度と同じ速度で降温したFe₈₈Nb₂Pr₅B₅なる組成の薄帯合金試料及びFe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料の残留磁化 (Ir)、角型比 (Ir/Is)、保磁力 (iHc) 及び最大磁気エネルギー積 ((BH)max) の昇温速度依存性を示す図である。また、bcc-Fe相の平均結晶粒径と磁気特性の関係を明確にするために、図5に、Fe₈₈Nb₂(Pr, Nd)₅B₅なる組成の薄帯合金試料のX線回折半価幅から求めたbcc-Fe相の平均結晶粒径と磁気特性の関係を示す。図1～

図5中、Taは熱処理時のアニール温度である。図1～図2中、一点鎖線は比較のためにbcc-Fe (pure-Fe) の格子定数と昇温速度との関係を示すものである。

【0044】表1～4及び図1～図2から明らかにように熱処理時における昇温速度を速くすることにより、973～1023Kで熱処理後におけるFe₈₈Nb₂Pr₅B₅なる組成の薄帯合金試料及びFe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料のbcc相の格子定数の昇温速度依存性は認められず、格子定数0.28665nmのpure-Feよりも大きい値を示しているが、bcc-Fe相の平均結晶粒径は昇温速度の上昇に伴なって微細化することが分る。また、最も速い昇温速度 (216K/分) で熱処理した薄帯合金試料では、Fe₈₈Nb₂Pr₅B₅なる組成の薄帯合金試料及びFe₈₈Nb₂Nd₅B₅な

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る組成の薄帯合金試料において、bcc相の結晶粒径は、それぞれ、約35nm、27~29nmの値となつた。

【0045】表1~表2及び図3から明らかなように熱処理時における昇温速度を速くすることにより、973Kの熱処理後のFe₈₈N₂P₅B₅なる組成の薄帯合金試料と、1023Kの熱処理後のFe₈₈N₂P₅B₅なる組成の薄帯合金試料が共にI_rおよびI_r/I_sの増加が認められ、その増加する割合は973Kの熱処理後のものよりも1023Kの熱処理後の薄帯合金試料において顕著であった。つぎに、iHcについては973Kの熱処理後のFe₈₈N₂P₅B₅なる組成の薄帯合金試料において昇温速度依存性は認められないが、1023KのFe₈₈N₂P₅B₅なる組成の薄帯合金試料においては昇温速度依存性が認められる。このようにI_r及びiHcが増加するのは、bcc-F_e相の平均結晶粒径が微細化することによる交換結合特性の向上に起因するものと考えられる。ただし、bcc-F_e相の平均結晶粒径の昇温速度依存性は、973Kで熱処理後の試料と1023Kの熱処理後の試料とで明確な差は認められず、1023Kの熱処理後の試料でI_r及びiHcの昇温速度依存性が大きいのは、bcc-F_e相の結晶粒径以外の要因があるものと推察される。つぎに、(BH)_{max}については973Kの熱処理後のFe₈₈N₂P₅B₅なる組成の薄帯合金試料と、1023Kの熱処理後のFe₈₈N₂P₅B₅なる組成の薄帯合金試料が共に昇温速度依存性が認められ、その増加する割合は1023Kの熱処理後の試料において顕著であった。

【0046】表2~表4及び図4から明らかなように熱処理時における昇温速度を速くすることにより、973Kの熱処理後のFe₈₈N₂N₅B₅なる組成の薄帯合金試料と1023Kの熱処理後のFe₈₈N₂N₅B₅なる組成の薄帯合金試料が共にI_rおよびI_r/I_sの増加が認められ、その増加する割合はFe₈₈N₂P₅B₅なる組成の薄帯合金試料ほど大きくなかった。つぎにiHcについては昇温速度依存性は殆ど認められない。つぎに、(BH)_{max}については、973Kの熱処理後のFe₈₈N₂N₅B₅なる組成の薄帯合金試料と1023Kの熱処理後のFe₈₈N₂N₅B₅なる組成の薄帯合金試料が共に昇温速度依存性が認められ、その増加する割合は1023Kの熱処理後の試料において顕著であった。Fe₈₈N₂N₅B₅なる組成の薄帯合金試料のI_rやiHcなどの磁気特性の昇温速度依存性が、Fe₈₈N₂P₅B₅なる組成の薄帯合金試料程明確でないのはbcc相の結晶粒径が全体的に微細であるため、bcc-F_e相の粒径に起因する効果が小さいものと考えられる。また、表1~表4の実施例中、残留磁化(I_r)は、最も小さいものでも1.26T(サンプルN_{o.10})、最も大きいものでは1.5T(サンプルN_{o.19})の大きな値が得られている。すなわち、各

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試料の密度が7.6g/cm³であることから換算すると、131emu/g~157emu/gとなり、130emu/g以上の大きな残留磁化が得られていることがわかる。

【0047】図5から明らかなようにFe₈₈N₂P₅B₅なる組成の薄帯合金試料とFe₈₈N₂N₅B₅なる組成の薄帯合金試料共にbcc-F_e相の結晶粒径が増加するに伴って、I_r/I_s、iHc及び(BH)_{max}が減少する傾向があることが判る。

【0048】上記実験結果より、組成が本発明の範囲であり、速い昇温速度で加熱し、973K~1023Kで熱処理して得られる薄帯合金試料は、高い硬磁気特性および平均結晶粒径100nm以下の微細結晶質相が析出した構造が得られることがわかった。また、昇温速度が10K/分以上では、bcc-F_e相の平均結晶粒径が小さくなり、I_r/I_s、iHc及び(BH)_{max}などの硬磁気特性が優れるので、本発明では熱処理時の昇温速度を10K/分以上とした。また、より高い磁気特性を得るためにには、より好ましくは昇温速度を36K/分とするのが良いことが分った。さらに昇温速度が100K/分以上ではFe₈₈N₂P₅B₅なる組成の薄帯合金試料及びFe₈₈N₂N₅B₅なる組成の薄帯合金試料において、bcc-F_e相の結晶粒径はそれぞれ約35~36nm、約26~32.5nmと、より微細化されており、特に、保磁力はそれぞれ約1.8~2.45kOe、約1.85~2.45kOeと優れていることから、本発明では熱処理時の昇温速度を好ましくは100K/分以上とした。

【0049】(実験例2)以下のようにして、急冷薄帯合金を熱処理するに際して保持時間を変更して硬磁性材料を作製した。上記実験例1と同様にして約20μmの厚さの急冷薄帯合金を作製し、さらにこの急冷薄帯合金を長さ2cmにカットした。ついで、長さ2cmの急冷薄帯合金を20本程度、1×10⁻⁵Pa以下の赤外線イメージ炉中において、昇温速度18K/分で加熱し、熱処理温度(アニール温度)973K~1073Kで3分~60分間保持する条件で熱処理して得られる薄帯合金試料の磁気特性に及ぼす影響について調べた。ここで得られた薄帯合金試料の組成は、いずれも本発明の範囲内にあるFe₈₄N₂N₅B₅S₁₂なる組成であった。結果を下記表5示す。また、図6にFe₈₄N₂N₅B₅S₁₂なる組成の薄帯合金試料の磁気特性の熱処理時間(保持時間)依存性を示す。また、図7~図9に、各熱処理条件で熱処理後のFe₈₄N₂N₅B₅S₁₂なる組成の薄帯合金試料のX線パターンの熱処理時間(保持時間)依存性を示す。ここで薄帯合金試料のX線回折パターンは、Cu-K α 線を用いたX線ディフラクトメーターにより解析した。

【0050】

【表5】

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熱処理温度 (K)	保持時間3分の ときの iHc(kOe)	保持時間10分の ときの iHc(kOe)	保持時間30分の ときの iHc(kOe)	保持時間60分の ときの iHc(kOe)
973	0.48	1.56	3.2	3.36
1023	3.44	3.5	3.09	2.89
1073	2.93	2.78	2.6	2.51

【0051】表5及び図6から明らかなように昇温速度18K/分でFe₈₄Nb₂Nd₇B₅Si₂急冷薄帯合金(2cm×20本)を熱処理する場合、保磁力が最大(3.5kOe)となったときの条件は、熱処理温度が1023Kで保持時間10分であることが判った。また、熱処理温度が973Kで保持時間60分と、熱処理温度が1023Kで保持時間3分の条件のとき、保磁力約3.38kOeの良好な硬磁気特性が得られていることが判った。また、熱処理温度が1073Kでの熱処理はすべての保持時間で保磁力が3kOe以下であった。

【0052】図7から明らかなように昇温速度18K/分、アニール温度973Kで熱処理後のFe₈₄Nb₂Nd₇B₅Si₂なる組成の試料のX線回折パターンは、保持時間が3分～30分と短い条件のとき、硬磁気特性に寄与しないFe₃Bが析出しており、硬磁気特性を示すNd₂Fe₁₄Bが殆ど析出していないために表5及び図6に示したように保磁力が高くないことが分る。一方、保持時間が60分と長い条件のとき、Nd₂Fe₁₄Bが析出しており、試料が良好な磁気特性を示す熱処理温度に十分に達し、高い保磁力が得られることが分る。図8から明らかなように昇温速度18K/分、アニール温度1023Kで熱処理後のFe₈₄Nb₂Nd₇B₅Si₂なる組成の試料のX線回折パターンは、すべての保持時間でNd₂Fe₁₄Bが析出していることが認められる。特に、保持時間が3分、10分のときには表5及び図6に示したように硬磁気特性が高くなっていることから、これに対して保持時間が30分、60分と長くなると硬磁気特性が減少しており、その理由は、保持時間3～10分の間で最も

* 適熱処理温度に十分達しており、この後更に熱処理をするとソフト磁性相(bcc-Fe相)の結晶粒が粒成長したためであると考えられる。図9から明らかなように昇温速度18K/分、アニール温度1073Kで熱処理後のFe₈₄Nb₂Nd₇B₅Si₂なる組成の試料のX線回折パターンは、すべての保持時間でNd₂Fe₁₄Bの析出が認められるが、表5及び図6に示したように硬磁気特性があまり高くなかったのは、熱処理温度自体が高くなり過ぎたためにソフト磁性相(bcc-Fe相)の結晶粒が粒成長したためであると考えられる。

【0053】(実験例3)以下のようにして、急冷薄帯合金を熱処理するに際して熱処理量(急冷薄帯合金の投入量)を変更して硬磁性材料を作製した。上記実験例1と同様にして約20μmの厚さの急冷薄帯合金を作製した。ついで、長さ2cmにカットした急冷薄帯合金20本(総重量約20mg)、2.5gの急冷薄帯合金4個(総重量10g)をそれぞれ1×10⁻⁵Pa以下の赤外線イメージ炉中において、上記実験例2で分った良好な硬磁気特性が得られる熱処理条件(①熱処理温度が973Kで保持時間60分、②熱処理温度が1023Kで保持時間3分、③熱処理温度が1023Kで保持時間10分、該①～③の熱処理条件において昇温速度はすべて18K/分)で熱処理して得られる薄帯合金試料の熱処理量が保磁力に及ぼす影響について調べた。ここで得られた薄帯合金試料の組成は、Fe₈₄Nb₂Nd₇B₅Si₂なる組成であった。結果を下記表6示す。

【0054】

【表6】

熱処理量 (投入量)	973K-保持時間60分 のときの iHc(kOe)	1023K-保持時間3分 のときの iHc(kOe)	1023K-保持時間10分 のときの iHc(kOe)
2cm×20本	3.36	3.44	3.5
2.5g×4個	3.73	3.33	3.49

【0055】表6から明らかなように急冷薄帯合金の投入量を増やしても上記①～③の熱処理条件で熱処理を行って得られたFe₈₄Nb₂Nd₇B₅Si₂の試料は、高い保磁力を持っていることから、高保磁力であるなどの硬

磁気特性が優れた硬磁性材料を製造するための適切な熱処理条件としては、硬磁性材料の組成がFe₈₄Nb₂Nd₇B₅Si₂である場合、①昇温速度18K/分であり、かつ熱処理温度973Kで60分間保持、②昇温速

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度18K/分であり、かつ熱処理温度1023Kで3分間保持、③昇温速度18K/分であり、かつ熱処理温度1023Kで10分間保持であることが分った。

【0056】(実験例4) $Fe_{88}Nb_2Pr_5B_5$ なる組成の急冷後の非晶質合金薄帯を昇温速度180K/分で加熱し、アニール温度750°Cで熱処理して得られた硬磁性材料の磁化の温度変化を調べた。また、 $Fe_{88}Pr_7B_5$ なる組成の急冷後の非晶質合金薄帯を昇温速度180K/分で加熱し、アニール温度650°Cで熱処理して得られた硬磁性材料の磁化の温度変化を調べた。その結果を図10に示す。図10は、 $Fe_{88}Nb_2Pr_5B_5$ なる組成の硬磁性材料と $Fe_{88}Pr_7B_5$ なる組成の硬磁性材料の磁化の温度変化を示す図である。図10に示されているように温度の上昇とともに磁化は2ステップで減少している。このことから、硬磁性材料の磁化に関与する相が2相存在していることが認められる。また、307°C付近で磁化の減少の度合いが変化していることから、この付近が $Fe_{14}Nd_2B$ 相のキュリー温度であり、800°C付近で磁化の減少の度合いが変化していることから、この付近が bcc -Fe相のキュリー温度であることが分る。なお、ここで非晶質相に起因する磁化のステップが見られないのは、磁化が低いことと体積分率が小さいことによるものと考えられる。

【0057】また、ここで得られた $Fe_{88}Nb_2Pr_5B_5$ なる組成の硬磁性材料と $Fe_{88}Pr_7B_5$ なる組成の硬磁性材料の磁化曲線の第2象限を図11に示す。図11に示されているように磁化曲線は、単一相からなる磁性材料と同様な、ステップの見られない磁化曲線となっており、微細なソフト磁性相とハード磁性相とが磁気的に結合した交換結合磁石が得られていることが分る。

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Ir及びiHcの温度係数(室温~約490K)

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*【0058】(実験例5) 各種組成の急冷薄帯合金を上述の実験例1と同様にして作製した。次いで、得られた急冷薄帯合金を 1×10^{-2} Pa以下の赤外線イメージ炉中において、昇温速度180K/分で加熱し、アニール温度1023Kで約3分間保持する条件で熱処理して薄帯合金試料(実施例)を得た。ここで得られた薄帯合金試料の組成は、いずれも本発明の範囲内にある $Fe_{88}Nb_2Pr_5B_5$ なる組成の薄帯合金、 $Fe_{76}Co_{10}Nb_2Pr_7B_5$ なる組成の薄帯合金、 $Fe_{66}Co_{20}Nb_2Pr_7B_5$ なる組成の薄帯合金、 $Fe_{84}Nb_2Pr_7B_5Si_2$ なる組成の薄帯合金であった。得られた実施例の薄帯合金試料について、VSM(振動試料型磁力計)を用い、10kOeの印加磁場中及び真空中で室温~約490Kにおける減磁曲線(第2象限)を図12~図14に示す。図13中、イはパーミアンス係数(p)が1.0(角柱形)である直線であり、ロはpが1.5(円盤形)である直線である。また、実施例の薄帯合金試料の磁気特性と温度との関係について、減磁曲線(第2象限)より求めた残留磁化(Ir)及び保磁力(iHc)の温度変化を図15に示した。また、得られた薄帯合金試料のIr及びiHcの温度係数と、p=1.5、p=1.0となる形状としたときのIrの温度係数を表7に示す。

【0059】比較例として従来のフェライト磁石とNd-Fe-B系磁石の磁気特性と温度との関係を図15に合わせて示す。これらの従来の磁石のIr及びiHcの温度係数を表7に合わせて示す。また、比較例としてBリッチのNd-Fe-B系の磁石のIr及びiHcの温度係数を表8に示す。

【0060】

【表7】

	硬磁性材料の組成	diIr/dT (%/K)	diHc/dT (%/K)	P=1.5のときの di/dT(%/K)	P=10のときの di/dT(%/K)
実 施 例	$Fe_{88}Nb_2Pr_5B_5$	-0.06	-0.43	-0.38	-0.12
	$Fe_{76}Co_{10}Nb_2Pr_7B_5$	-0.02	-0.28	-0.20	-0.10
	$Fe_{66}Co_{20}Nb_2Pr_7B_5$	-0.02	-0.36	-0.33	-0.08
	$Fe_{84}Nb_2Pr_7B_5Si_2$	-0.02	-0.32	-0.17	-0.05
比 較 例	$Fe_{77}Nd_{15}B_8$	0.16	0.4		
	$(Fe_{0.9}Co_{0.1})_{77}Nd_{15}B_8$	-0.11	-0.35	--	--
	フェライト磁石	-0.18	--	--	--

【0061】

【表8】

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Ir及びiHcの温度係数

	硬磁性材料の組成	dIr/dT (%/K)	diHc/dT (%/K)	温度範囲 (K)
比 較 例	Nd ₅ Fe _{78.5} B _{18.5}	-0.043	-0.398	297-413
	Nd ₅ Fe _{70.5} Co ₃ Ga ₃ B _{18.5}	-0.074	-0.336	297-413
	Nd ₃ Dy ₂ Fe _{70.5} Co ₃ Ga ₁ B _{18.5}	-0.048	-0.361	297-413
	Nd _{3.5} Dy ₁ Fe ₇₃ Co ₃ Ga ₁ B _{18.5}	-0.08	-0.39	348付近

【0062】図15及び表7から実施例の薄帯合金試料ならびに比較例の磁石は、温度の上昇とともにIr及びiHcが減少する傾向が認められる。iHcの温度係数(d iHc/dT)については、実施例のFe₈₈N₂B₅P₅なる組成の試料が-0.43%/Kであり、比較例のNd-Fe-B系磁石の値(-0.43%/K)に近い値であるが、CoやSiを添加した実施例の薄帯合金試料では-0.28~-0.36%/Kと比較例のNd-Fe-B系磁石よりも温度係数の絶対値が小さい値であることが認められる。このようにCoを添加することによりiHcの温度係数の絶対値が減少するのは、ハード磁性相のキュリー温度が上昇することに起因するものと考えられる。また、Siを添加すると全体の保磁力が上がるため、結果的にiHcの温度係数の絶対値が減少する。

【0063】次に、Irの温度係数(dIr/dT)については、実施例のFe₈₈N₂B₅P₅なる組成の試料が-0.06%/Kであり、比較例のNd-Fe-B系磁石(Fe₇₇Nd₅B₈なる組成の磁石、(Fe_{0.9}C_{0.1})₇₇Nd₁₅B₈なる組成の磁石)の値が-0.11~-0.16%/Kであるのに比べて温度係数の絶対値が低くなっていることが認められる。これは比較例の磁石では磁化に関与する相がハード磁性相のみであるに対して、実施例の薄帯合金試料では、ハード磁性相と、磁化の温度変化率の小さいソフト磁性相(bcc-Fe相)が混在したナノ複相組織を有しているからであると考えられる。また、CoやSiを添加した実施例の薄帯合金試料では、Irの温度係数が-0.02%/Kであり、温度係数の絶対値が大幅に小さい値であることが認められる。表7及び表8から実施例の薄帯合金試料のIr及びiHcの温度係数は、BリッチのNd-Fe-B系の磁石のIr及びiHcの温度係数と同じ程度かそれ以下の値であることが認められる。図13からFe₆₆Co₂₀N₂B₇P₅なる組成の試料は、p=10以上の領域では磁化の温度変化が小さく、温度特性が優れていることが分る。

【0064】図16は、実施例の薄帯合金試料をp=10となる形状で使用したときの各温度でのIrの値を図12~図14に示した減磁曲線より求めたものである。また、比較のために従来のSm-Co磁石とNd-Fe-B系磁石(Nd₂Fe₁₄Bなる組成)をp=10とな

る形状で使用したときのIrの温度変化を図16に合わせて示す。図17は、本発明の組成の範囲内にあるFe₈₈N₂B₅P₅なる組成の焼結バルク(合金圧密体)試料及びFe₈₈N₂B₂P₇B₅なる組成の薄帯合金試料のパーミアンス係数と温度係数との関係を示すものである。また、比較のために従来のNd-Fe-B系磁石(Nd₂Fe₁₄Bなる組成)のパーミアンス係数と温度係数との関係を図17に合わせて示す。

【0065】表7及び図16~図17からp=10となる形状で使用したとき、実施例のFe₈₈N₂B₅P₅なる組成の試料は温度係数が-0.12%/Kであり、従来のNd-Fe-B系磁石の温度係数と同じ程度であるが、Siを添加した実施例のFe₈₄N₂B₂P₇B₅Si₂なる組成の試料は-0.05%/Kであり、Coを添加した実施例のFe₆₆Co₂₀N₂B₇P₅なる組成の試料は-0.08%/Kと温度係数の絶対値が小さい値を示していることが分る。また、p=10となる形状で使用したとき、実施例の薄帯合金試料、特に、Fe₈₄N₂B₂P₇B₅Si₂なる組成の試料は、300~430K程度の実用温度範囲において温度係数の絶対値が小さく、比較例のSm-Co系磁石と同じ程度の優れた温度特性を有しており、また、比較例のNd-Fe-B系磁石よりも温度特性が優れていることが分る。図17から実施例の試料はパーミアンス係数が10以上で使用したとき、比較例のNd-Fe-B系磁石よりも温度係数の絶対値が小さく、温度特性が優れていることが分る。

【0066】(実験例6)実験例1と同様にして作製した急冷薄帯合金を1.3×10⁻³トール以下の赤外線イメージ炉において、昇温速度(α)3~180K/分で加熱し、973K~1023Kで約180秒間保持する条件で熱処理して得られる薄帯合金試料の磁気特性およびナノ結晶構造に及ぼす影響について調べた。ここで得られた薄帯合金試料の組成は、本発明の範囲内にあるFe₈₈N₂B₅P₅なる組成の薄帯合金であった。得られた薄帯合金試料の構造はX線ディフラクトメータ及び高分解型透過型電子顕微鏡(TEM)にて調べ、磁気特性はVSM(振動試料型磁化測定装置)を用いて薄帯合金試料の長手方向に室温にて1.5Tの印加磁場をかけることにより求めた。

【0067】図18は、1023Kの熱処理温度で18

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0秒保持した後、急冷した（赤外線イメージ炉中で炉冷した）Fe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料の減磁曲線（第2象限）の昇温速度依存性を示すグラフである。図18から明らかなように昇温速度が本発明の範囲内にある180K/分、18K/分である実施例のものは、比較例のもの（昇温速度が3K/分）に比べてI、Hともに大きくなっていることが認められることから、実施例のものは（BH）_{max}も大きいことがわかる。図19は、1023Kの熱処理温度で180秒保持した後、急冷した（赤外線イメージ炉中で炉冷した）Fe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料のIr、Ir/I_s、iHc及び（BH）_{max}の昇温速度依存性を示す図である。図19から明らかなようにFe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料は、熱処理時における昇温速度を速くすることにより、Ir、Ir/I_s、iHc、（BH）_{max}が顕著に増加していることが認められる。従って、1023Kの熱処理温度で180秒保持した後、急冷したFe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料においても昇温速度依存性が認められる。図20は、熱処理時の昇温速度を3～180K/分、保持時間を180秒とし、その後急冷した（赤外線イメージ炉中で炉冷した）Fe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料のIr、Ir/I_s及びiHcの熱処理温度（保持温度）依存性を示す図である。図20から明らかなように各薄帯合金試料とも1020Kの保持温度で熱処理した方が良い特性が得られており、特に、昇温速度が180K/分で、保持温度が970～1070Kで熱処理した実施例のものは、昇温速度が3K/分である比較例のものに比べて優れた磁気特性が得られていることがわかる。

【0068】図21は、熱処理時の昇温速度を3～180K/分、保持温度を1023K、保持時間を180秒とし、その後急冷して得られた各Fe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料の磁化の温度変化を示す図である。図21から明らかなように熱処理時の昇温速度が異なる各薄帯合金試料の磁化の温度変化は、温度の上昇とともに殆ど同様に減少していることがわかる。これは、磁化が熱処理時の昇温速度に殆ど依存しないことを示唆している。図22は、熱処理時の保持温度を1023K、保持時間を180秒とし、その後急冷したFe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料のbcc-Fe相とNd₂Fe₁₄B相の平均結晶粒径の昇温速度依存性を示す図である。図22中のbcc-Fe(TEM)、Nd₂Fe₁₄B(TEM)はTEM写真からそれぞれ求めた粒径であり、bcc-Fe(XRD)はX線回折のグラフから求めた粒径である。図22から明らかなように薄帯合金試料のbcc-Fe相とNd₂Fe₁₄B相とともに昇温速度を速くするにつれて平均結晶粒径が小さいものが得られており、特に、Nd₂Fe₁₄B相はbcc-Fe相より平均結晶粒径が小さいうえ、bcc-Fe相

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より昇温速度に大きく依存していることがわかる。従って、Fe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料の磁気特性の昇温速度依存性は結晶粒径の微細化に起因していることがわかる。それは、Nd₂Fe₁₄B相の平均結晶粒径が小さくなれば、bcc-Feの粒子とNd₂Fe₁₄Bの粒子が隣り合う確率、すなわちbcc-Feの粒子とNd₂Fe₁₄Bの粒子が結合している部分が多くなり、ソフト磁性相(bcc-Fe)とハード磁性相(Nd₂Fe₁₄B)の交換結合が行われ易くなるために交換結合特性が向上するからである。

【0069】図23は、液体急冷法により得られたFe₈₈Nb₂Nd₅B₅なる組成の非晶質合金薄帯試料の各昇温速度におけるDSC(示差走査熱量測定)曲線を示す図である。図23中、各DSC曲線における最初のピークの始めの部分がbcc-Fe相の結晶化温度(T_{x1})であり、2番目のピークの始めの部分がNd₂Fe₁₄B相の結晶化温度(T_{x2})である。図24(a)は、図23に示した各昇温速度におけるDSC曲線のbcc-Fe相のT_{x1}と、Nd₂Fe₁₄B相のT_{x2}を示すものであり、(b)は図23に示した各昇温速度におけるDSC曲線のNd₂Fe₁₄B相のT_{x2}とbcc-Fe相のT_{x1}の差(DT_x=T_{x2}-T_{x1})を示すものである。図22～図24より明らかなように熱処理時の昇温速度を速くするにつれてNd₂Fe₁₄B相のT_{x2}とbcc-Fe相のT_{x1}の差(DT_x)が小さくなっていることから、DT_xが小さければ小さい程bcc-Fe相とNd₂Fe₁₄B相の双方の平均結晶粒径を微細化することができる事がわかる。それは、DT_xが小さくなる程、bcc-Fe相とNd₂Fe₁₄B相を同時に結晶化できる傾向が強くなるためにどちらかの結晶が粗大化するのを防止することができるからである。

【0070】

【発明の効果】以上説明したように本発明に係わる硬磁性材料は、Fe、Co、Niのうち1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含み、急冷直後において非晶質相を主相とする合金が10K/分以上の昇温速度で熱処理されてなり、保磁力が1kOe以上であるものであるので、上記合金中に析出する微細結晶質相のbcc-Fe相とR₂Fe₁₄B相の平均結晶粒径を微細化することができる。さらに、R₂Fe₁₄B相はbcc-Fe相より平均結晶粒径が小さいうえ、bcc-Fe相より昇温速度に大きく依存するので、熱処理時の昇温速度を10K/分以上とすることにより、bcc-Feの粒子とR₂Fe₁₄Bの粒子が隣り合う確率が多くなり、ソフト磁性相(bcc(体心立方構造)-Fe)とハード磁性相(R₂Fe₁₄B)の交換結合が行われ易くなるために交換結合特性が向上し、優れた硬磁気特性が得られる。さらに、本発明に係わる硬磁性材料は、希土類元素Rの含有量を少なくしても良好な硬磁気特性が得られるので、比較的低い製造コ

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ストで製造することができる。

【0071】本発明に係わる硬磁性材料は、急冷直後において非晶質相を主相とする合金が10K/分以上の昇温速度で熱処理されてなり、保磁力1kOe以下のソフト磁性相と保磁力1kOe以上のハード磁性相とをそれぞれ10vol(体積)%以上含んでなる保磁力が1kOe以上であるものであるので、ソフト磁性相とハード磁性相の中間の特性を備えることができ、磁化の温度係数の絶対値も小さいものとすることができる。本発明に係わる硬磁性材料は、急冷直後において非晶質相を主相とする合金が10K/分以上の昇温速度で熱処理されてなり、キュリー温度が600°C以上の磁性相とキュリー温度が600°C以下の磁性相とをそれぞれ10vol(体積)%以上含んでなる保磁力が1kOe以上であるものであるので、ソフト磁性相とハード磁性相の中間の特性を備えることができ、磁化の温度係数の絶対値も小さいものとすることができる。

【0072】上記急冷直後において非晶質相を主相とする合金を10K/分以上の昇温速度で熱処理後に得られる硬磁性材料で、平均結晶粒径100nm以下の微細結晶質相を主相として含むものにあっては、ソフト磁性相とハード磁性相の交換結合特性が優れ、硬磁気特性が優れる。本発明に係わる硬磁性材料において、上記急冷直後において非晶質相を主相とする合金が100K/分以上の昇温速度で熱処理されてなるものにあっては、平均結晶粒径の小さい(均一な微細組織)を実現できる。本発明に係わる硬磁性材料において、特に、パーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値が0.10%/K以下としたものにあっては、温度変化が小さいことを必要とするセンサーなどの製品に使用できる。

【0073】本発明に係わる硬磁性材料によれば、保磁力が2kOe以上の硬磁性材料を実現できる。また、本発明に係わる硬磁性材料によれば、飽和磁化(I_s)に対する残留磁化(I_r)の割合(I_r/I_s)が、0.6以上の硬磁性材料を実現でき、従って、高い残留磁化(I_r)を実現することができ、高い最大磁気エネルギー積((BH)_{max})を持つ硬磁性材料を得ることができる。本発明の硬磁性材料にあっては、組成をTxMyRzBwとし、組成比を示すx, y, z, wは原子%で、50≤x、0≤y≤15、3≤z≤20、3≤w≤20なる関係を満足するものとし、かつ、残留磁化(I_r)が100emu/g以上のものとすることにより、希土類元素の濃度が低くても急冷状態で良好な非晶質相が得られ、その後の10K/分以上の昇温速度で熱処理されることより硬磁気特性を付与する化合物が析出されるので、低コストで優れた硬磁気特性を有する硬磁性材料が得られる。ここでの組成式中の組成比を示すx, y, z, wは、8.6≤x≤9.2、0.5≤y≤3、3≤z≤7、3≤w≤7なる関係を満足することにより、より優

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れた硬磁気特性を得ることができる。

【0074】本発明の硬磁性材料にあっては、組成をTxMyRzBwEvとし、組成比を示すx, y, z, w, vは原子%で、50≤x、0≤y≤10、3≤z≤15、3≤w≤20、0≤v≤10なる関係を満足するものとすることにより、さらに、耐食性をも備えることができる。ここでの組成式中の組成比を示すx, y, z, w, vは原子%で、8.0≤x≤9.2、1≤y≤5、4≤z≤10、3≤w≤7、0≤v≤5なる関係を満足することにより、より優れた硬磁気特性を得ることができる。本発明に係わる硬磁性材料においては、Si元素がT元素置換で0.5~5原子%添加されることにより、あるいはT元素中にFe以外にCoが含まれることにより、パーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値が0.10%/K以下のものを得ることができ、温度特性を向上させることができる。従って本発明の硬磁性材料にあっては、磁気式ロータリーエンコーダやポテンショメータなどのセンサ、アクチュエータ、スピーカ、モータなどの各種の装置に使用される磁石材料として有用であり、製造コストの低減を図ることができる。

【0075】本発明の硬磁性材料の製造方法にあっては、Fe, Co, Niのうち1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含み、非晶質相を主相とする合金を液体急冷法により作製した後、該合金を10K/分以上の昇温速度で熱処理する工程を備えることにより、R₂Fe₁₄B相の結晶化温度とbcc-Fe相の結晶化温度の差が小さくなり、bcc-Fe相とNd₂Fe₁₄B相を同時に結晶化できる傾向が強くなるためにどちらかの結晶相が粗大化するのを防止することができ、上記合金中に析出する微細結晶質相のbcc-Fe相とR₂Fe₁₄B相の平均結晶粒径を微細化することができる。さらに、R₂Fe₁₄B相はbcc-Fe相より平均結晶粒径が小さいうえ、bcc-Fe相より昇温速度に大きく依存するので、熱処理時の昇温速度を10K/分以上とすることにより、bcc-Feの粒子とR₂Fe₁₄Bの粒子が隣り合う確率が多くなり、ソフト磁性相(bcc(体心立方構造)-Fe)とハード磁性相(R₂Fe₁₄B)の交換結合が行われ易くなるために交換結合特性が向上し、硬磁気特性が優れた硬磁性材料を提供することができる。また、希土類元素の含有量を、従来の希土類磁石よりも少なくしても優れた硬磁気特性が得られるので、比較的低い製造コストで高性能の硬磁性材料を製造することができる。

【0076】さらに、本発明に係わる硬磁性材料の製造方法にあっては、特に、上記の非晶質相を主相とする合金を100K/分以上の昇温速度で熱処理することにより、(BH)_{max}が大きく、均一な微細結晶が析出した硬磁性材料を好適に得ることができる。また、本発明に係わる硬磁性材料の製造方法にあっては、特に、上記の

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非晶質相を主相とする合金にSiをT元素置換で0.5～5原子%添加した合金を用いることにより、パーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値が0.10%／K以下の硬磁性材料を得る方法として好適に用いることができる。

【図面の簡単な説明】

【図1】 973K～1023Kで熱処理後におけるFe₈₈Nb₂P₇B₅なる組成の試料のbcc-Fe相の格子定数及び平均結晶粒径の昇温速度依存性を示す図である。

【図2】 973K～1023Kで熱処理後におけるFe₈₈Nb₂Nd₅B₅なる組成の試料のbcc-Fe相の格子定数及び平均結晶粒径の昇温速度依存性を示す図である。

【図3】 973K～1023Kの熱処理温度で5分間保持した後、昇温速度と同じ速度で降温したFe₈₈Nb₂P₇B₅なる組成の試料の磁気特性の昇温速度依存性を示す図である。

【図4】 973K～1023Kの熱処理温度で5分間保持した後、昇温速度と同じ速度で降温したFe₈₈Nb₂Nd₅B₅なる組成の試料の磁気特性の昇温速度依存性を示す図である。

【図5】 Fe₈₈Nb₂(Pr, Nd)₅B₅なる組成の試料のbcc-Fe相の平均結晶粒径と磁気特性の関係を示す図である。

【図6】 Fe₈₄Nb₂Nd₇B₅Si₂なる組成の試料の磁気特性の熱処理時間(保持時間)依存性を示す図である。

【図7】 昇温速度18K／分、アニール温度973Kで熱処理後のFe₈₄Nb₂Nd₇B₅Si₂なる組成の試料のX線パターンの熱処理時間(保持時間)依存性を示す図である。

【図8】 昇温速度18K／分、アニール温度1023Kで熱処理後のFe₈₄Nb₂Nd₇B₅Si₂なる組成の試料のX線パターンの熱処理時間(保持時間)依存性を示す図である。

【図9】 昇温速度18K／分、アニール温度1073Kで熱処理後のFe₈₄Nb₂Nd₇B₅Si₂なる組成の試料のX線パターンの熱処理時間(保持時間)依存性を示す図である。

【図10】 Fe₈₈Nb₂P₇B₅なる組成の硬磁性材料とFe₈₈Pr₇B₅なる組成の硬磁性材料の磁化の温度変化を示すグラフである。

【図11】 Fe₈₈Nb₂P₇B₅なる組成の硬磁性材料とFe₈₈Pr₇B₅なる組成の硬磁性材料の磁化曲線の第2象限示すグラフである。

【図12】 Fe₇₆Co₁₀Nb₂P₇B₅なる組成の薄帯合金試料の302.5K～489Kにおける減磁曲線(第2象限)を示すグラフである。

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【図13】 Fe₆₆Co₂₀Nb₂P₇B₅なる組成の薄帯合金試料の308K～471Kにおける減磁曲線(第2象限)を示すグラフである。

【図14】 Fe₈₄Nb₂P₇B₅Si₂なる組成の薄帯合金試料の301.5K～477Kにおける減磁曲線(第2象限)を示すグラフである。

【図15】 実施例の薄帯合金試料ならびに比較例の磁石の磁気特性と温度との関係を示す図である。

【図16】 実施例の薄帯合金試料ならびに比較例の磁石をそれぞれp=10となる形状で使用したときIrの温度変化を示す図である。

【図17】 本発明の組成の範囲内にあるFe₈₈Nb₂Nd₅B₅なる組成の焼結バルク(合金圧密体)、Fe₈₆Nb₂P₇B₅なる組成の薄帯合金ならびに従来のNd-Fe-B系磁石のパーミアンス係数と温度係数との関係を示す図である。

【図18】 1023Kの熱処理温度で180秒保持した後、急冷したFe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料の減磁曲線(第2象限)の昇温速度依存性を示すグラフである。

【図19】 1023Kの熱処理温度で180秒保持した後、急冷したFe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料のIr、Ir/Is、iHc及びBH_{max}の昇温速度依存性を示す図である。

【図20】 热処理時の昇温速度を3～180K／分、保持時間を180秒とし、その後急冷したFe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料のIr、Ir/Is及びiHcの熱処理温度(保持温度)依存性を示す図である。

【図21】 热処理時の昇温速度を3～180K／分、保持温度を1023K、保持時間を180秒とし、その後急冷して得られた各Fe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料の磁化の温度変化を示す図である。

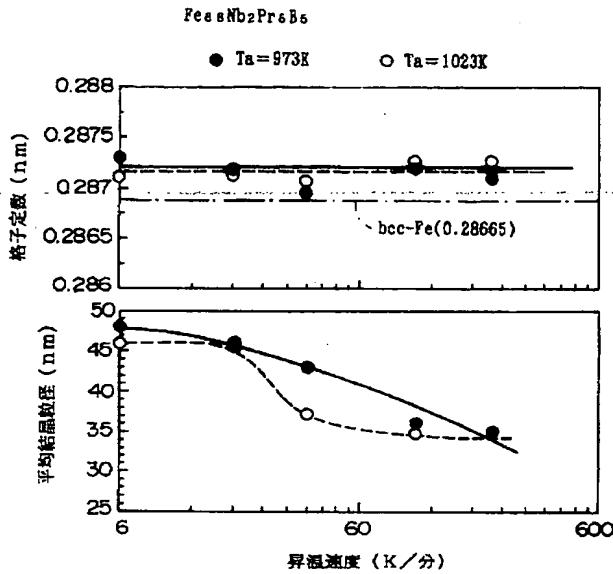
【図22】 热処理時の保持温度を1023K、保持時間を180秒とし、その後急冷したFe₈₈Nb₂Nd₅B₅なる組成の薄帯合金試料のbcc-Fe相とNd₂Fe₁₄B相の平均結晶粒径の昇温速度依存性を示す図である。

【図23】 急冷法により得られたFe₈₈Nb₂Nd₅B₅なる組成の非晶質合金薄帯試料の各昇温速度におけるDSC(示差走査熱量測定)曲線を示す図である。

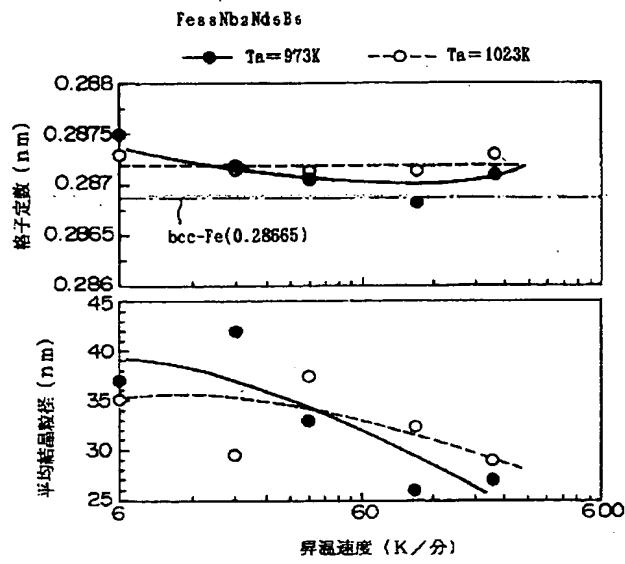
【図24】 (a)は、図23に示した各昇温速度におけるDSC曲線のbcc-Fe相の結晶化温度(T_{x1})と、Nd₂Fe₁₄B相の結晶化温度(T_{x2})を示す図であり、(b)は図23に示した各昇温速度におけるDSC曲線のNd₂Fe₁₄B相のT_{x2}とbcc-Fe相の結晶化温度T_{x1}の差(DT_x=T_{x2}-T_{x1})を示す図である。

(18)

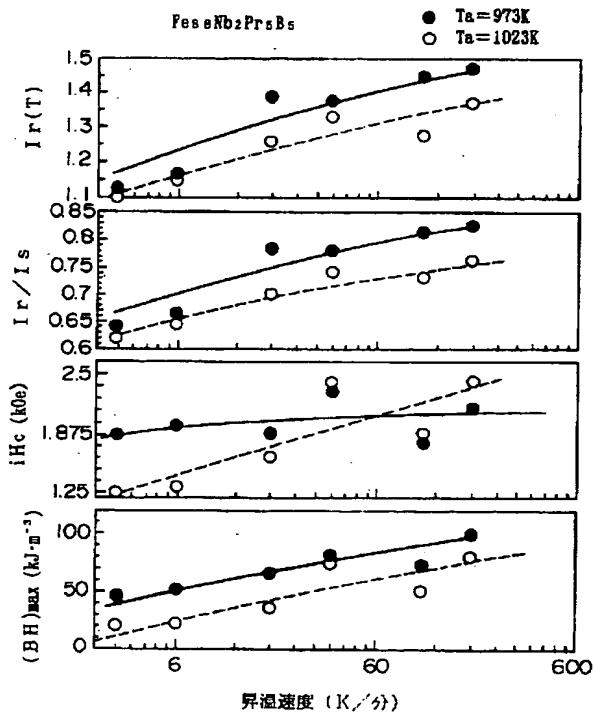
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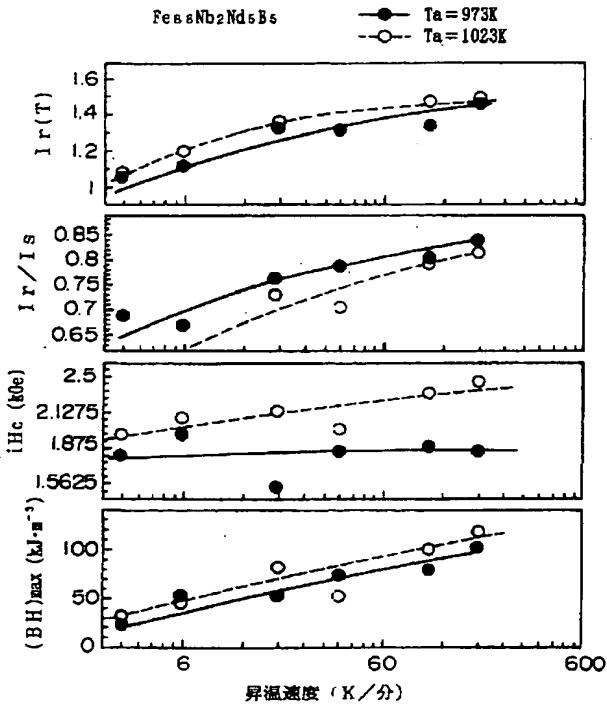
【図2】



【図3】

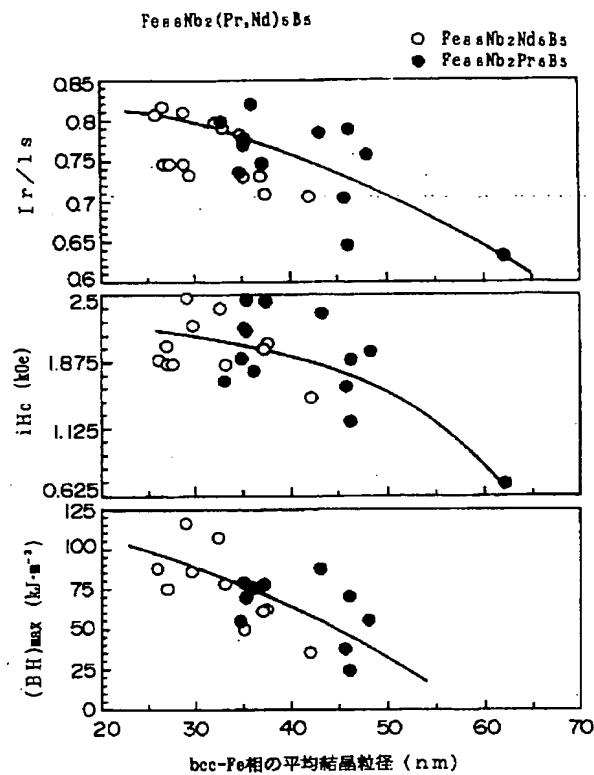


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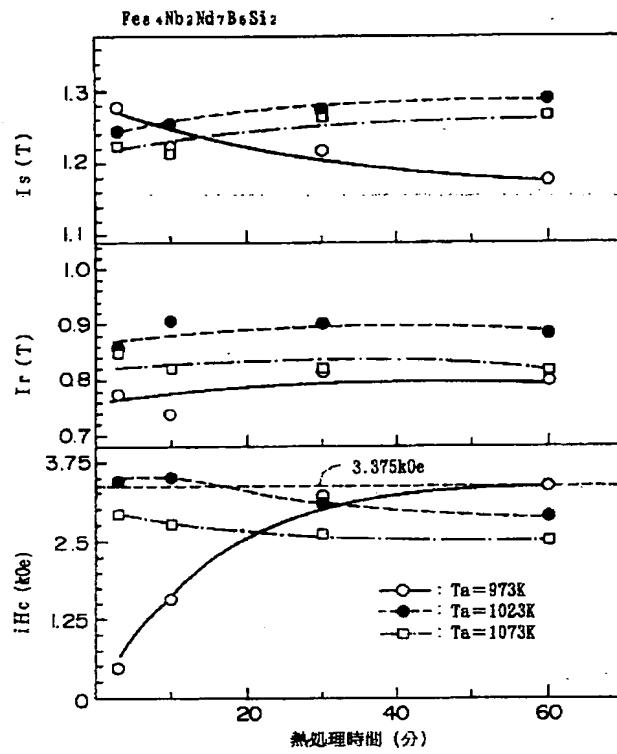


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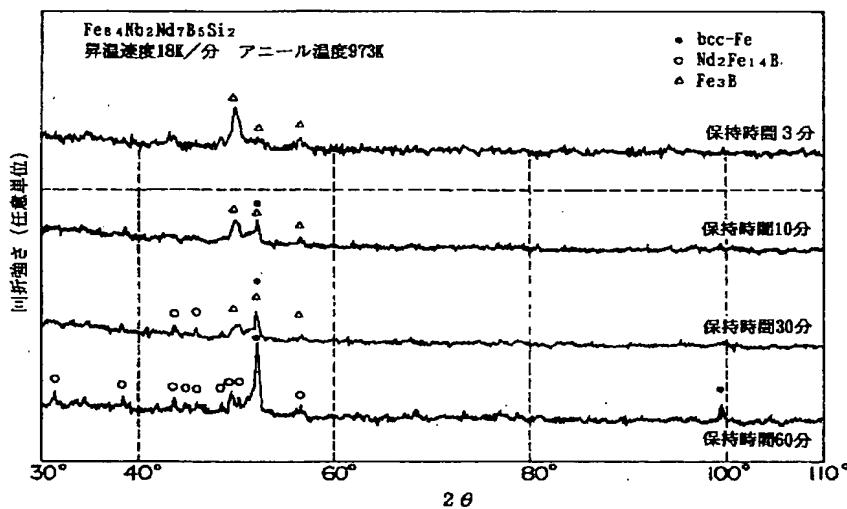
【図5】



【図6】

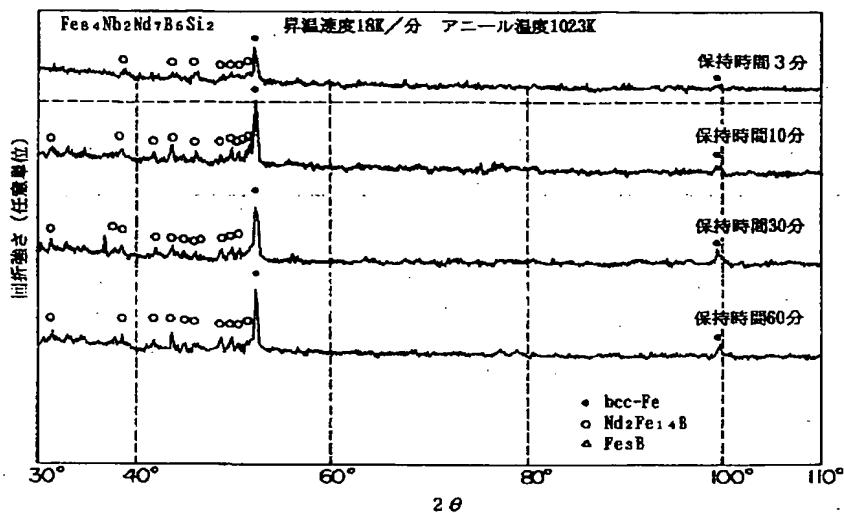


【図7】

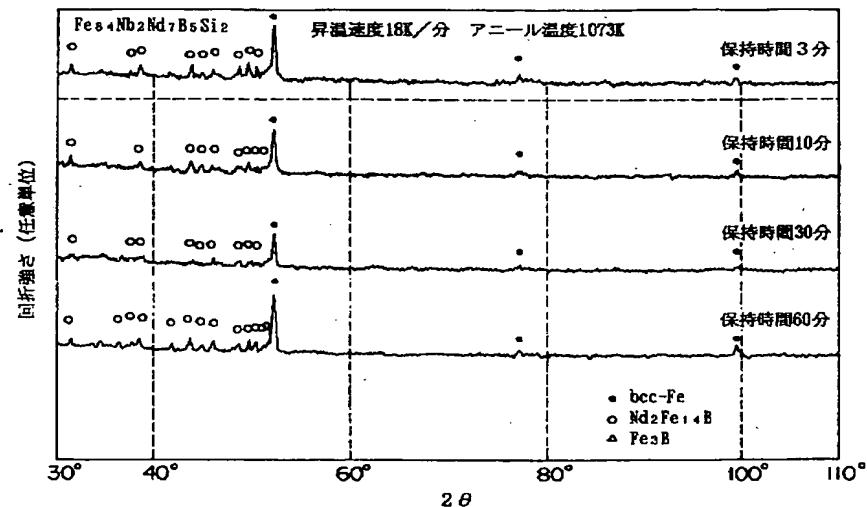


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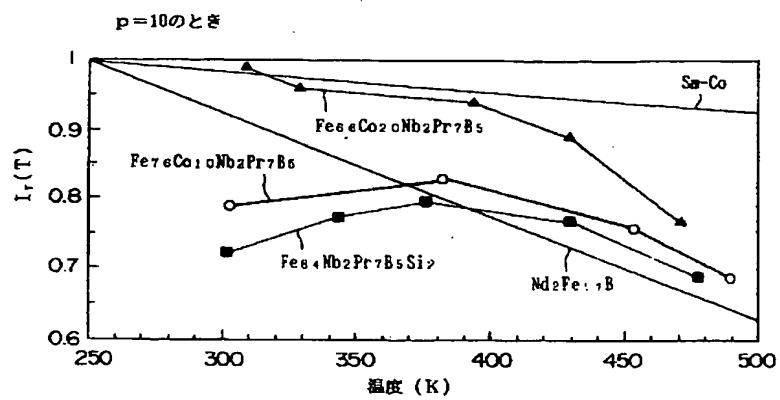
【図8】



【図9】

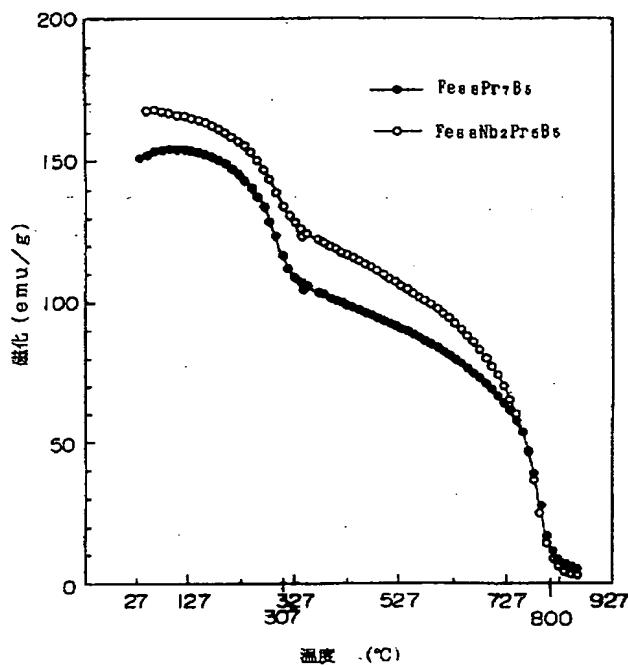


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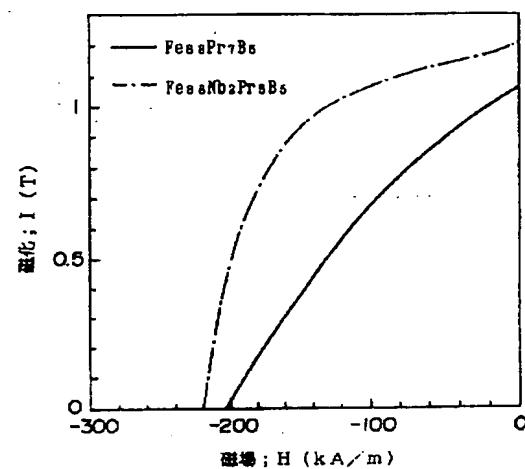


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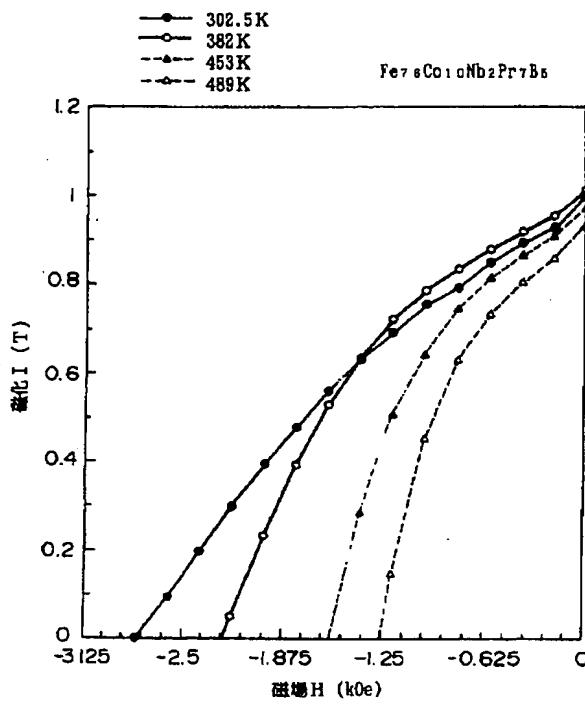
【図10】



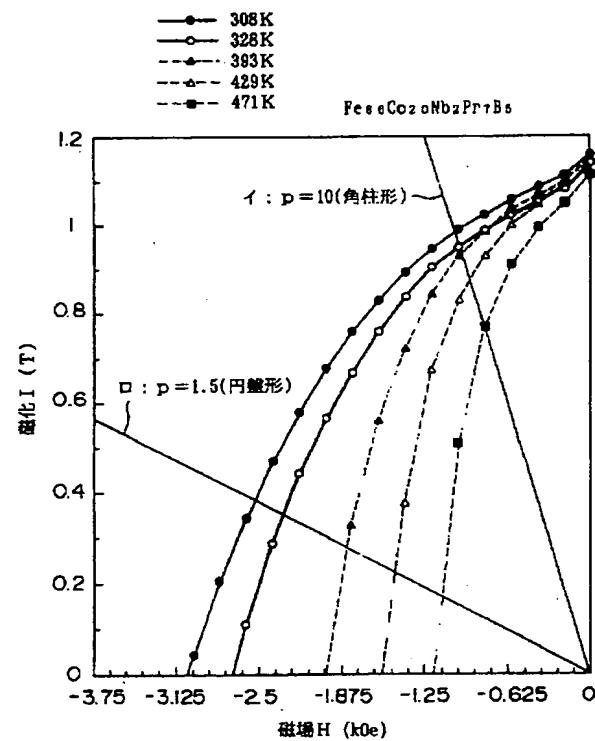
【図11】



【図12】

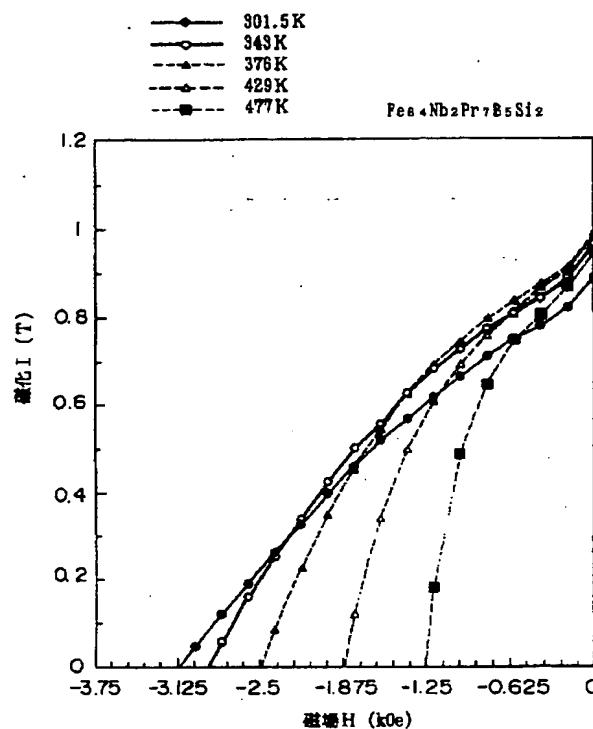


【図13】

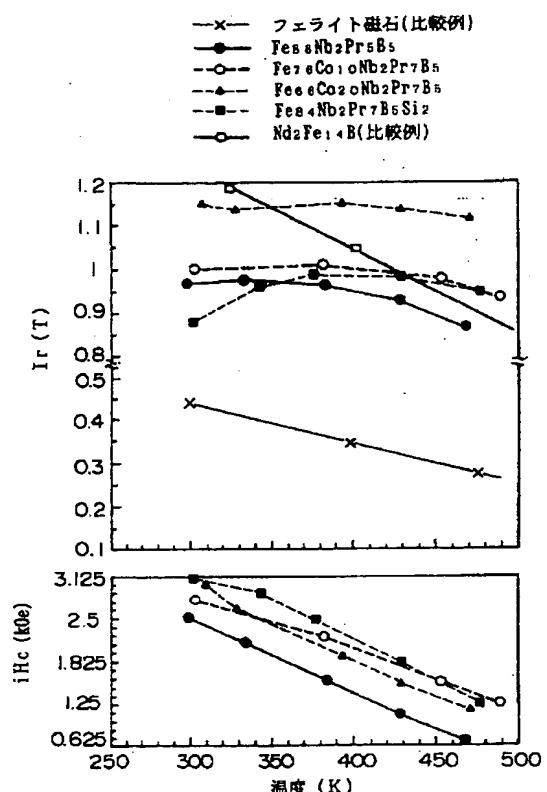


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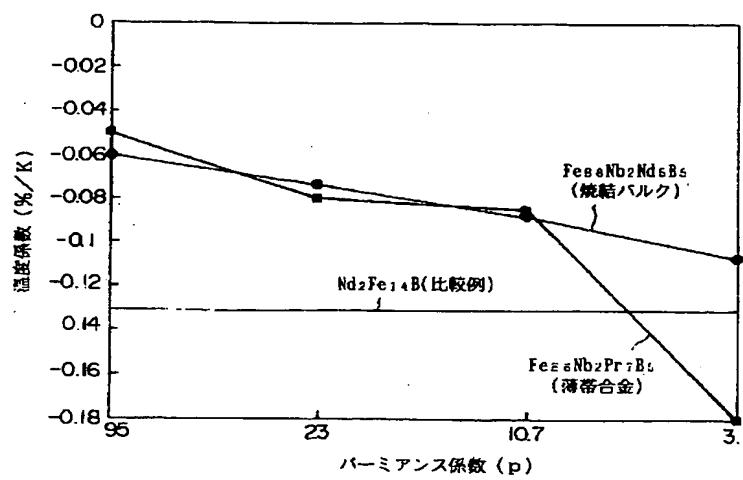
【図14】



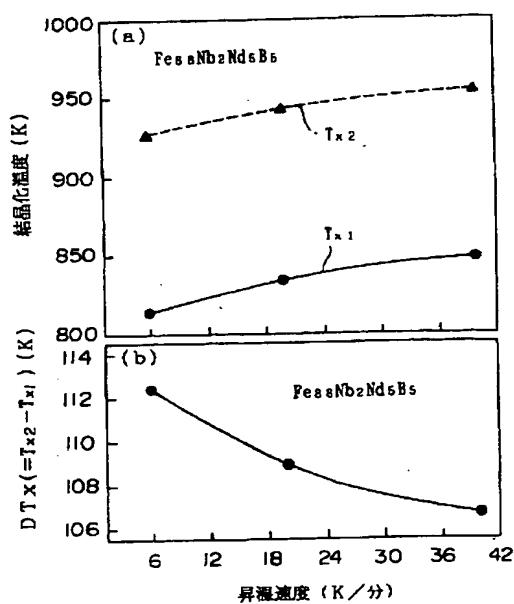
【図15】



【図17】

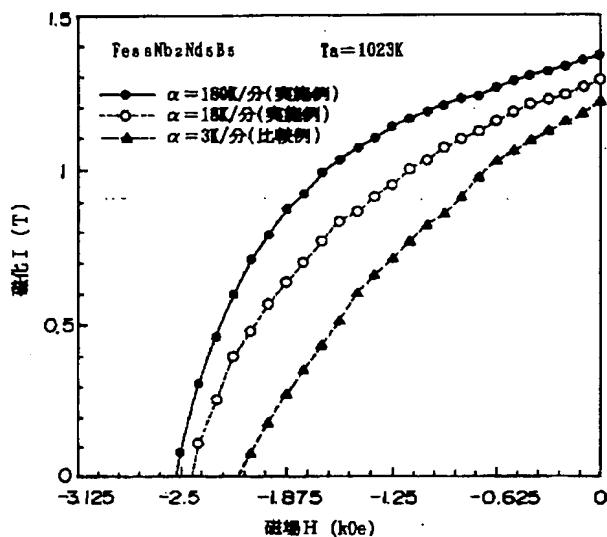


【図24】

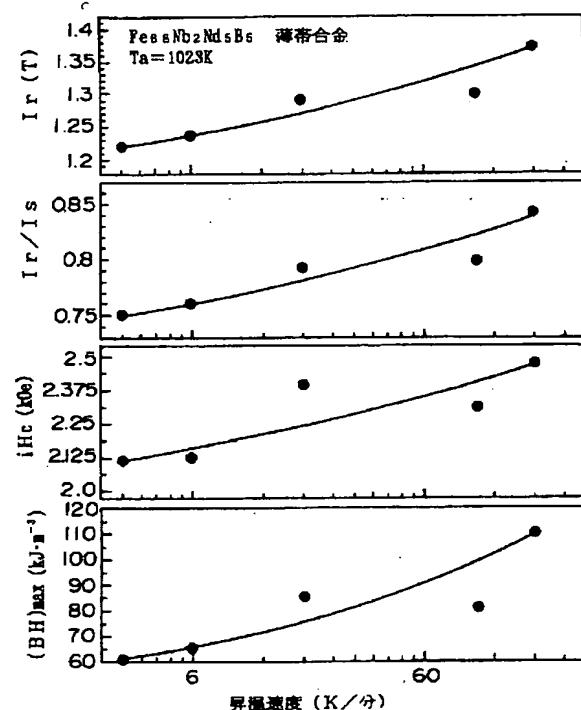


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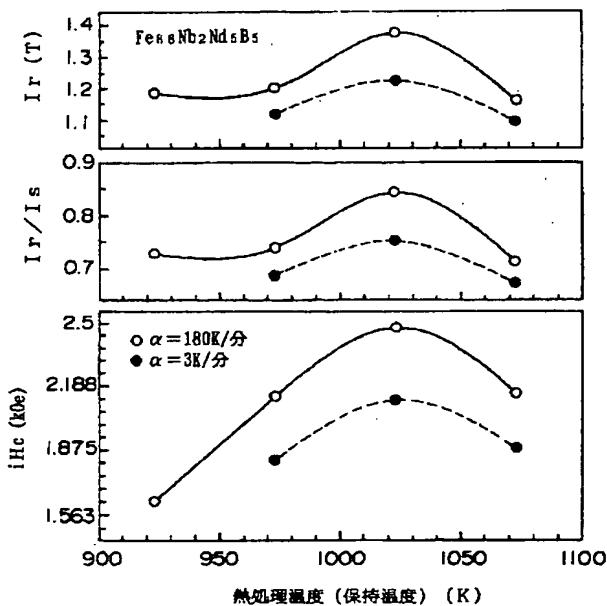
【図18】



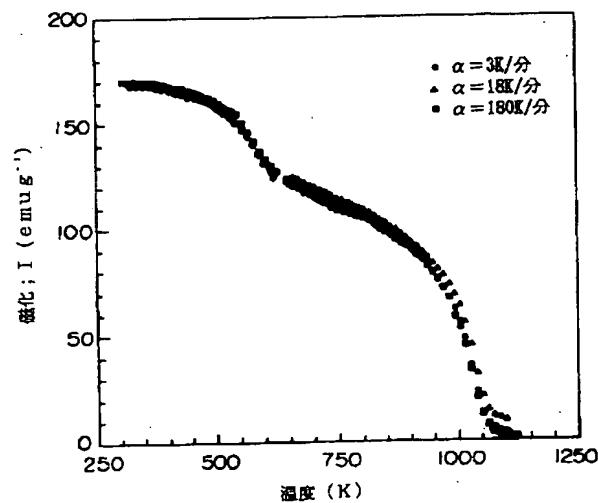
【図19】



【図20】

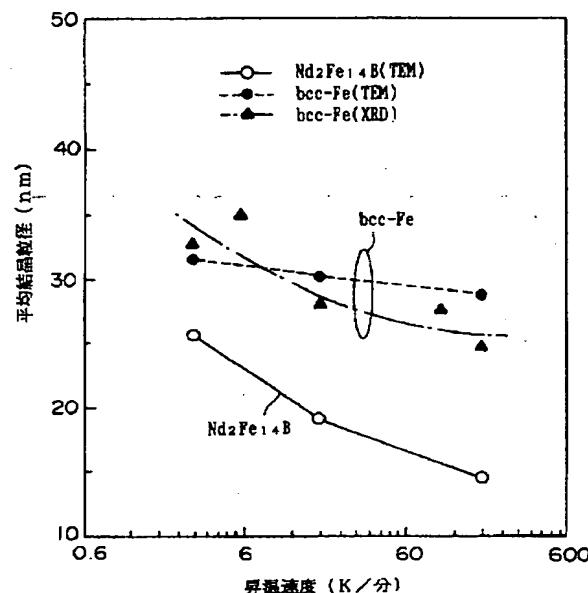


【図21】

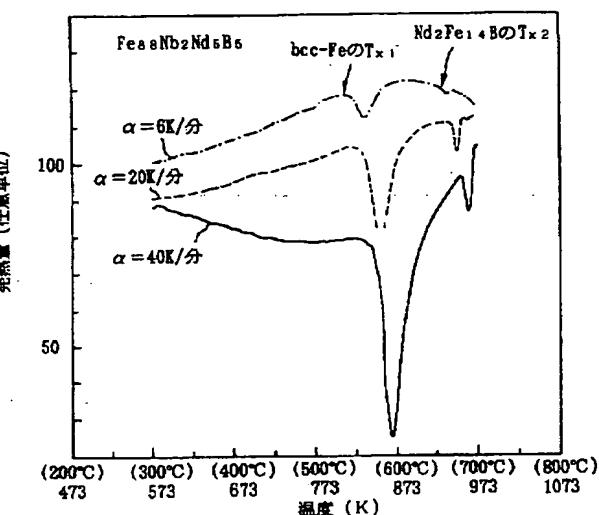


(24)

【図22】



【図23】



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